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ADVANCED TECHNIQUES FOR IMPROVING
LASER OPTICAL SURFACES

Charles B. Willingham

Raytheon Company

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This program is a study of surface-finishing techniques considered to be capable of improving the surface quality of laser optical materials. A variety of conventional and "superpolishing" techniques will be developed for single- crystal and polycrystalline potassium chloride and calcium fluoride, and poly- crystalline zinc selenide. (Continued)		

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During the first six months of the program, experimental studies of all polishing techniques began. Acceptable conventional polishing techniques for polycrystalline calcium fluoride and zinc selenide were developed, and preliminary grinding steps of the process were identified as requiring further study. Bowl-feed "superpolishing" was shown to improve the surface quality of conventionally polished zinc selenide and calcium fluoride substantially.

During the second report period, grinding damage was shown to be effectively removed from polycrystalline fluoride and selenide surfaces by removal by means of polishing a layer somewhat thicker than the diameter of the abrasive used to generate the ground surface.

Zinc sulfide powders were evaluated as infrared-transparent abrasives for potassium chloride and found to be inferior to alumina. Since chemical polishing has been found to remove abrasives from the surfaces, transparent abrasives no longer appear to be required and this part of the experimental program was terminated.

Light scattering measurements demonstrated that ion milling could be used to clean surfaces prior to deposition of optical coatings without seriously degrading them, but that more extensive material removal sharply increased scattering at angles close to the specular direction.

Chemical polishing studies of all materials were begun. An ammonium chloride solution was found to be a promising chemical-mechanical polish for calcium fluoride. An approximately 0.2 molar alkaline solution of potassium ferricyanide was chosen as an optimum chemical polishing agent for zinc selenide. Etch rates of single and polycrystalline potassium chloride in hydrochloric acid were found to be on the order of 10 micrometers per minute. This is likely to be too rapid for controlled etching of large halide optics and attempts to decrease the etch rate by additions to the acid have begun. Profilometer traces of a polycrystalline surface from which approximately 10 micrometers had been removed by hydrochloric acid etching showed typical grain-to-grain variations in height of only approximately 500 angstroms. This sort of variation should be quite acceptable on the optical surfaces.

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TECHNICAL REPORT SUMMARY

Optical elements of new high power lasers must eventually handle power densities approaching the fundamental breakdown limits of their component materials. To operate at these levels, the optical elements must be free of such damage-inducing defects as embedded absorbing abrasive particles and field-concentrating pores and microcracks, perhaps as small as 100 angstroms. These are new demands of optical materials which are normally required only to be free of major light-scattering defects (and to have an accurate figure).

This program is an eighteen-month study of surface finishing techniques considered to be capable of improving the surface quality of laser optical materials. Chemical and chemical-mechanical polishing, ion-beam polishing, bowl-feed and continuously recycled abrasive "superpolishing" techniques are being evaluated for single crystal and polycrystalline potassium chloride and calcium fluoride, and polycrystalline zinc selenide. Conventional abrasive polishing procedures for all materials are being optimized and the use of zinc sulfide in various forms as an infrared-transparent abrasive for potassium chloride is being explored.

During the first report period, preliminary experimentation in all the project areas began and techniques for conventional polishing and bowl-feed "superpolishing" of calcium fluoride and zinc selenide were developed. Cleavage damage produced during grinding of the polycrystalline materials was identified as a potential source of defects in conventionally polishing surfaces.

During this report period, systematic studies of the polishing of ground selenide and fluoride surfaces demonstrated that the removal of a surface layer somewhat greater in thickness than the particle size of the abrasive originally used to grind the surface essentially eliminated grinding damage as a source of defects in conventionally polished material.

Glycerol triacetate (triacetin), a compound first utilized by workers at the Naval Weapons Center, was used as the slurry vehicle in conventional and bowl-feed polishing of potassium chloride. Surfaces were prepared which were marginally improved over those previously produced using ethylene glycol media.

Samples of pure zinc sulfide and zinc sulfide hardened by gallium additions were prepared by precipitation and used to polish potassium chloride. Powders so produced were composed of roughly spherical particles approximately one micrometer in diameter which produced generally poorer polished surfaces than did alumina abrasives. No correlation between the presence of gallium additions in the sulfide abrasives and either polished surface quality or rate of stock removal could be made. Zinc sulfide was being evaluated as an infrared-transparent abrasive material, the presence of which in a polished chloride surface would not cause preferential laser damage. Since chemical polishing procedures appear to remove the (opaque) alumina abrasives, there seemed to be little need to develop transparent abrasives further and work in the area was terminated.

Ion-beam polishing was shown to produce grain-to-grain height variations in polycrystalline zinc selenide and calcium fluoride which were approximately ten percent of the total thickness of material removed. This etching increases light scattering from the surfaces. Scattering measurements were made on zinc selenide surfaces from which various thicknesses of material had been milled. The removal of layers comparable to those which might be removed during an ion milling cleaning operation prior to vacuum deposition of an optical coating were found to increase the surface scattering by, at most, 15 percent.

Chemical polishing procedures were explored for all materials. A one-molar aqueous solution of ammonium chloride was shown to be a promising chemical-mechanical polish for calcium fluoride. The solution produced some differential grain etching in polycrystalline samples. Since it produces very perfect surfaces on appropriately-oriented grains, variations of the solution are being pursued further.

A variety of oxidizing agents was used to etch zinc selenide. Of these, a 5:1 dilution of the alkaline ferricyanide etch first reported by Hughes Research Laboratories was chosen as the chemical polishing agent for the optimized selenide polishing procedure. The diluted etch attacks the surface more slowly than the undiluted and is easier to control.

The rates at which hydrochloric acid etches single and polycrystalline potassium chloride were found to be on the order of 10 micrometers per minute. Considering that this material will most likely be used as components of carbon dioxide lasers, this corresponds to a removal rate of one wavelength per minute. Although lesser thicknesses of material will probably be removed in the final etching step, this high rate is likely to be too high to permit controlled etching of large polycrystalline optical elements. A one-to-one dilution of hydrochloric acid in triacetin was used as an etch and found to decrease the etch rate by an order of magnitude below that for hydrochloric acid alone, but it produced an irregularly etched surface.

A profilometer trace was made of a polycrystalline potassium chloride surface from which approximately 10 micrometers of material had been etched by hydrochloric acid. Although the surface itself was far from flat, grain-to-grain surface height variations produced by orientation-dependent etching were on the order of only 500 angstroms. This variation should be acceptable for any conceivable halide optical surfaces. The etch appears to be sufficiently nonpreferential, but is too rapid.

During the final six months of the program, chemical polishing of calcium fluoride and potassium chloride will be emphasized. A major effort will be made to develop a mechanical-chemical procedure which can be scaled to polish large polycrystalline potassium chloride optical elements. Conventional polishing studies will continue at a lower level of activity and emphasize the identification of sources of variability in the conventionally polished surfaces.

FOREWORD

This report was prepared by Raytheon Company, Research Division, under Contract No. F19628-73-C-0280 entitled, "Advanced Techniques for Improving Laser Optical Surfaces." This work is supported by the Advanced Research Projects Agency and is monitored by the Air Force Cambridge Research Laboratories, Bedford, Massachusetts.

At Raytheon Company, Dr. C.B. Willingham is the principal investigator of the project. R. Cosgro and F. Taylor are performing the experimental polishing work. Surface scatter and absorption measurements are being made by Dr. T. Kohane and T. Varitimos. Ion beam polishing work was performed by C. Dunnrowicz; profilometer measurements and ATR spectra were taken by M. Schapira. Others contributing to the project include Drs. P.A. Miles and D.W. Readey. This report has been given an internal number of S-1721.

1.0 INTRODUCTION

The goal of this project is to develop techniques which will produce the highest possible laser damage thresholds on surfaces of optical components in lasers operating in the 3-5 and 10.6 micrometer spectral ranges. Until the advent of high-power lasers, the important criteria for laser optical component surfaces were the absence of major light-scattering scratches together with accurate fabrication of the optical figure. Surfaces required to transmit high energy densities have additional constraints. They must be free of embedded particles of absorbing material, polishing abrasives, and free of field-concentrating features such as pores and microcracks, perhaps as small as 100 angstroms.

The double constraint of optical figure and surface perfection makes it likely that the techniques sought will require some form of abrasive polishing to establish the figure while producing the least possible surface damage, followed by a treatment to remove the surface damage and remnant abrasive particles. Chemical etching, chemical-mechanical polishing, and ion-beam polishing are candidate processes for the latter step. The final surface will in general be used as a substrate for an antireflection or other optical coating. As such, it must be free of chemical or particulate residues from the final cleaning or etching procedures.

Techniques such as bowl-feed and continuously-recycled abrasive polishing, in which the finest abrasive particles are continuously fed to the workpieces, produce the most nearly perfect abrasively-polished surfaces and are being explored as the final abrasive polishing step.

Since it is most probable that an optimum surface preparation technique will be particular only to one material or at best to a class of materials (alkaline earth halides, for example), this project considers the surface finishing of three materials: zinc selenide, calcium fluoride, and potassium chloride. These materials not only represent three material classes, but are themselves important laser optical materials.

Further, although single crystals of potassium chloride and calcium fluoride will be studied, polycrystalline specimens are being emphasized; high strength or large-area components will most likely be polycrystalline.

Polished surfaces are inspected and characterized by a variety of direct techniques including optical microscopy and scanning electron microscopy and by indirect methods such as transmission electron microscopy of surface replicas and surface light scattering measurements. Ultimately, laser damage measurements will be made to compare the most promising preparation methods.

During the course of this investigation, the application of the various finishing and evaluation techniques to the study materials will be made in a systematic manner. Results of the experimental work, both positive and negative, will be reported in progress. Optimum procedures for the finishing of each study material will be selected and discussed in detail in the final report. Effective optical finishing techniques have historically been regarded as proprietary by those possessing them. An important aspect of funded research in this area is the generation of widely distributed discussions of optimized procedures for these important laser optical materials.

This is the second semiannual report of an eighteen-month project. During the first six months, work in all project areas began. Acceptable conventional polishing techniques for zinc selenide and potassium chloride were developed. Bowl-feed "superpolishing" of calcium fluoride and zinc selenide was initiated. Measurements of light scattering from bowl-feed and conventionally-polished specimens demonstrated a factor-of-three improvement of bowl-feed polished zinc selenide and an order-of-magnitude improvement for calcium fluoride. Defects in bowl-feed polished surfaces were considered to be related to preceding abrasive polishing steps which are being studied further.

This report contains results obtained in four areas. Conventional polishing studies demonstrated that grinding-induced cleavage damage can

be eliminated from developing surfaces. A chemical polishing procedure was adopted for use with zinc selenide and developmental work done on procedures for the other materials. The use of zinc sulfide as an abrasive for potassium chloride was evaluated, and work defining the utility of ion beam polishing in the area was continued.

During the final six months of the project, two major project areas will be pursued; development of chemical polishes for potassium chloride and calcium fluoride will be continued, and a concentrated effort will be made to integrated results of this development into a mechanical and chemical procedure for polycrystalline potassium chloride which can be scaled to large sizes. Conventional polishing studies will continue at a lower level emphasizing the identification and elimination of sources of variability in the process.

2.0 RESULTS

2.1 Abrasive Polishing

2.1.1 Conventional polishing, zinc selenide and calcium fluoride

Conventional abrasive polishing techniques for zinc selenide and calcium fluoride were developed during the first report period. Aluminum oxide abrasives and soft pitch laps produced the highest quality surfaces on both materials. Parallel experiments performed on zinc selenide by Itek Corporation under subcontract developed the same optimized procedure. The surface quality produced by these "optimized" procedures proved to be variable, and efforts to identify and eliminate the sources of the variability were undertaken during the second report period. During the grinding operations which precede polishing, material is removed from these crystalline pieces at least partially by cleavage. It is possible that cleavage cracks produced during the grinding operation are driven into the surface to a greater depth than are fractures which are generated during grinding of glass. These latter are typically contained in a defective surface region which is roughly twice as thick as the diameter of the grinding abrasives used to generate the ground glass surface. To assess the contribution of remnant cleavage cracks to defects in polished surfaces, series of "standard ground surfaces" were produced on calcium fluoride and zinc selenide. The polishing of these surfaces was followed as detailed below.

Blocks of polycrystalline calcium fluoride specimens and of four 1.5-inch diameter zinc selenide specimens were polished to conventional B-alumina surfaces. The specimens were then ground with a Microgrit alumina grinding abrasive until a layer several times the nominal particle size of the grinding abrasive in thickness had been removed from their surfaces. This procedure was used to produce ground surfaces which were characteristic of the action of only a single grinding abrasive.

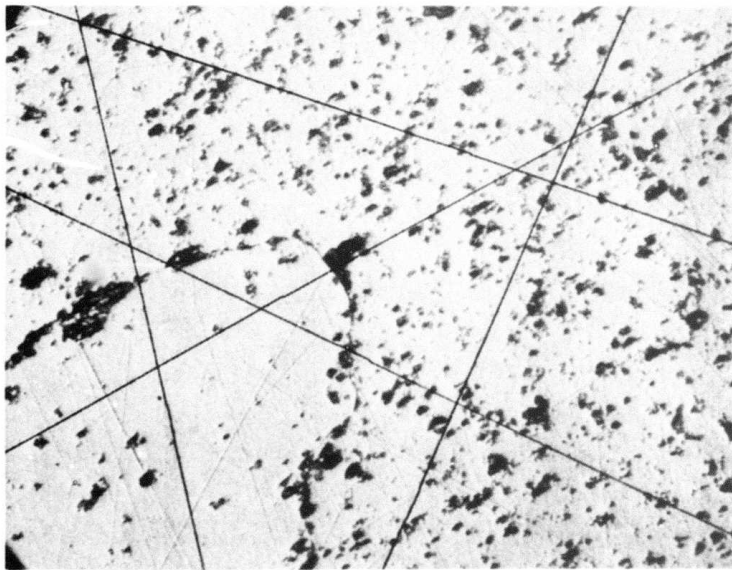
Ground surfaces were then polished with 'A'-type alumina (0.3 micrometer nominal particle size). The polishing was interrupted periodically, the thickness of the material removed was measured with a dial gauge (accurate to plus or minus approximately two micrometers), and photomicrographs of

three randomly selected areas on the surface were taken. Surface defect densities were then determined by counting the number of remnant pits in the photographs and by computing the average surface area fraction covered by the pits. This second measure, useful only above a few percent coverage, is computed by measuring the fractional length of lines drawn randomly across the photographs which intersect pits.

Microstructural changes which accompany the polishing of ground polycrystalline calcium fluoride surfaces generated by five-micrometer nominal grain diameter abrasives are summarized in Fig. 1. Figure 2 details the polishing of a polycrystalline fluoride surface generated with 12-micrometer alumina. Defect densities taken from the photographs are correlated with polishing time and material removal in Figs. 3 and 4.

Both polishing experiments may be seen to proceed in essentially the same way. The fractional area covered by grinding pits falls below one percent or so at about the same time that a material layer approximately equal to one grinding abrasive particle diameter is removed. Beyond this point, the larger pits have essentially been eliminated and the smaller pits are distributed more or less randomly over the photograph area. The random distribution of these smallest defects probably indicates that they are not caused by remnant cleavage damage. Where lesser amounts of stock have been removed, defect densities vary more strongly from grain to grain in the microstructure and reflect variations in the orientation of cleavage planes with respect to the polished surfaces. Figure 1b, taken of the 5-micrometer surface after approximately three micrometers of stock had been removed, illustrates the point. The surface at the top of the photograph caps a grain from which essentially all grinding damage has been removed.

Unfortunately, these experiments were not carried out to include the removal of many times the grinding compound diameter. This was done in the zinc selenide experiment described below. We can conclude, however, that although grinding damage is related to cleavage in calcium fluoride and that it varies in depth from grain to grain in polycrystalline material, the removal of a few grinding compound diameters from the developing surface by polishing should also remove the grinding damage.

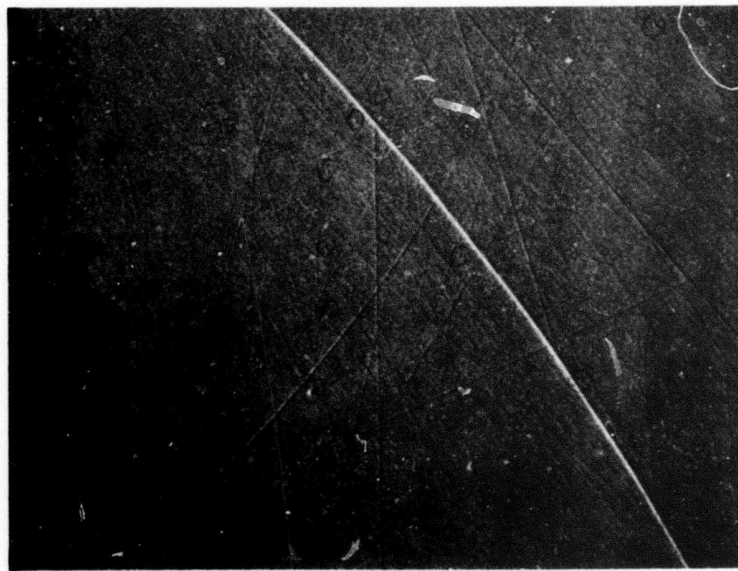


a) Time: 10 Minutes. Removal: Unmeasured.

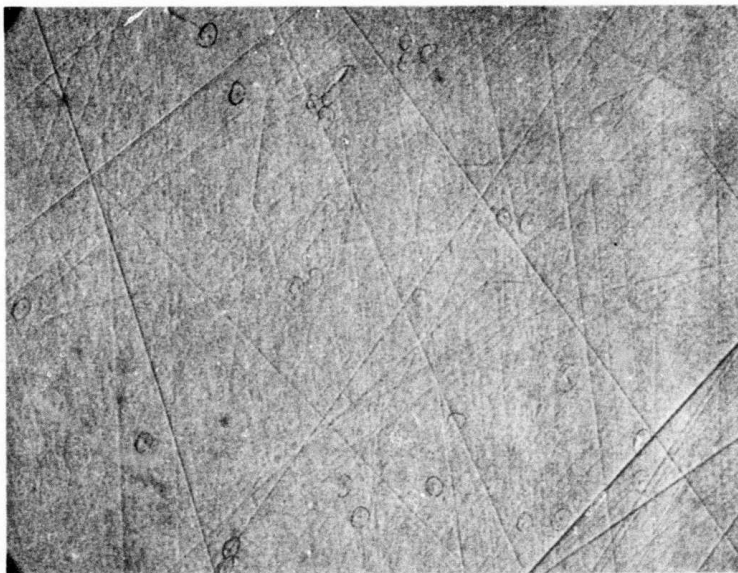


b) Time: 70 Minutes. Removal: 3 μm .

Fig. 1 Microstructures Produced During Polishing of Ground Polycrystalline Calcium Fluoride Surface Produced by Five-Micrometer Alumina Grinding Abrasive. 187X

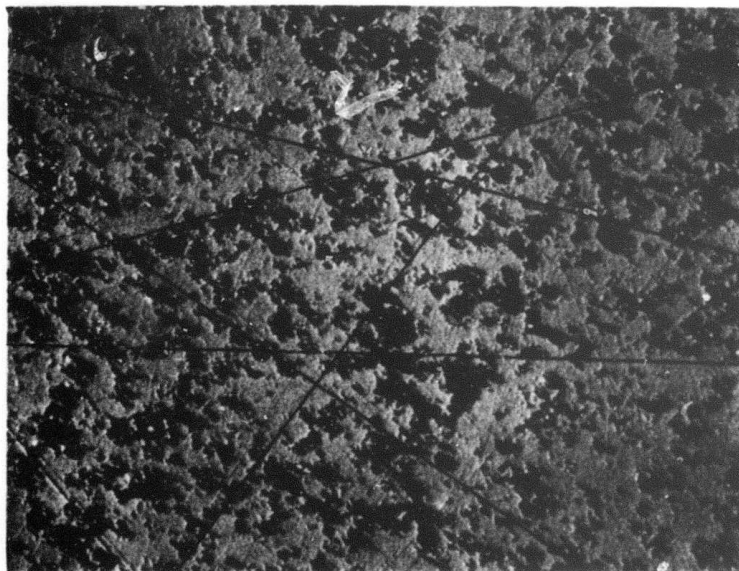


c) Time: 130 Minutes. Removal: 5 μm .

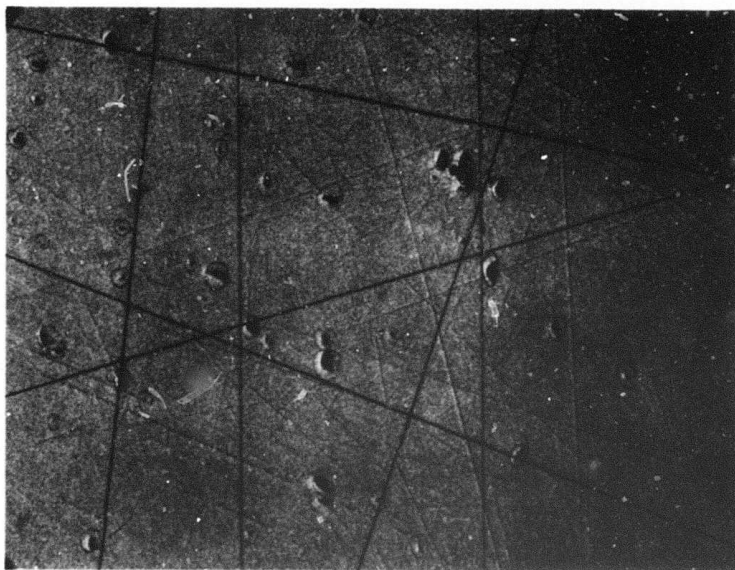


d) Time: 280 Minutes. Removal: 8.4 μm .

Fig. 1 (Cont'd)

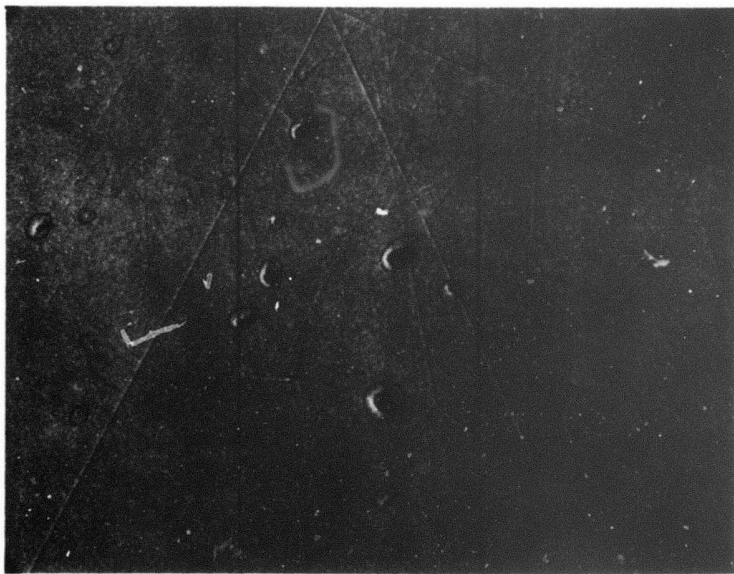


a) Time: 10 Minutes. Removal: 3 μm



b) Time: 180 Minutes. Removal: 8 μm

Fig. 2 Microstructure Produced During Polishing of Ground Polycrystalline Calcium Fluoride Surface Produced by Twelve-Micrometer Alumina Grinding Abrasive. 187x

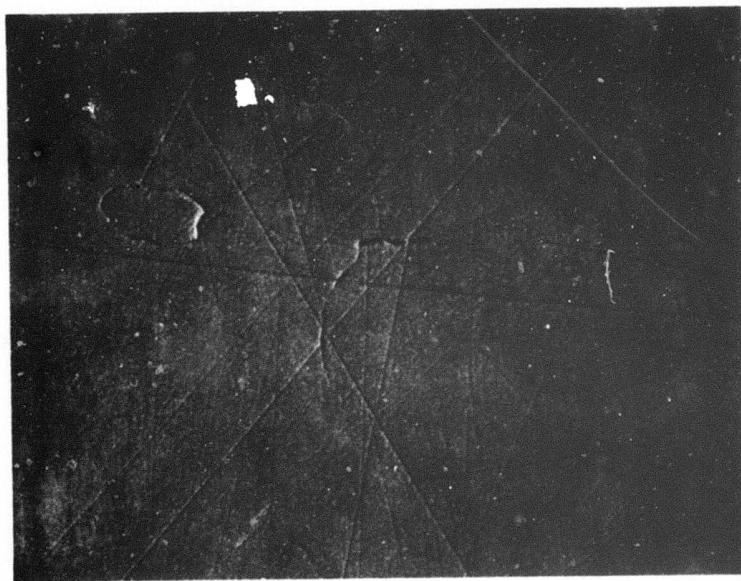


c) Time: 240 Minutes. Removal: 12 μm .



d) Time: 360 Minutes. Removal: 15 μm .

Fig. 2 (Cont'd)



e) Time: 480 Minutes. Removal: 17 μm .

Fig. 2 (Cont'd)

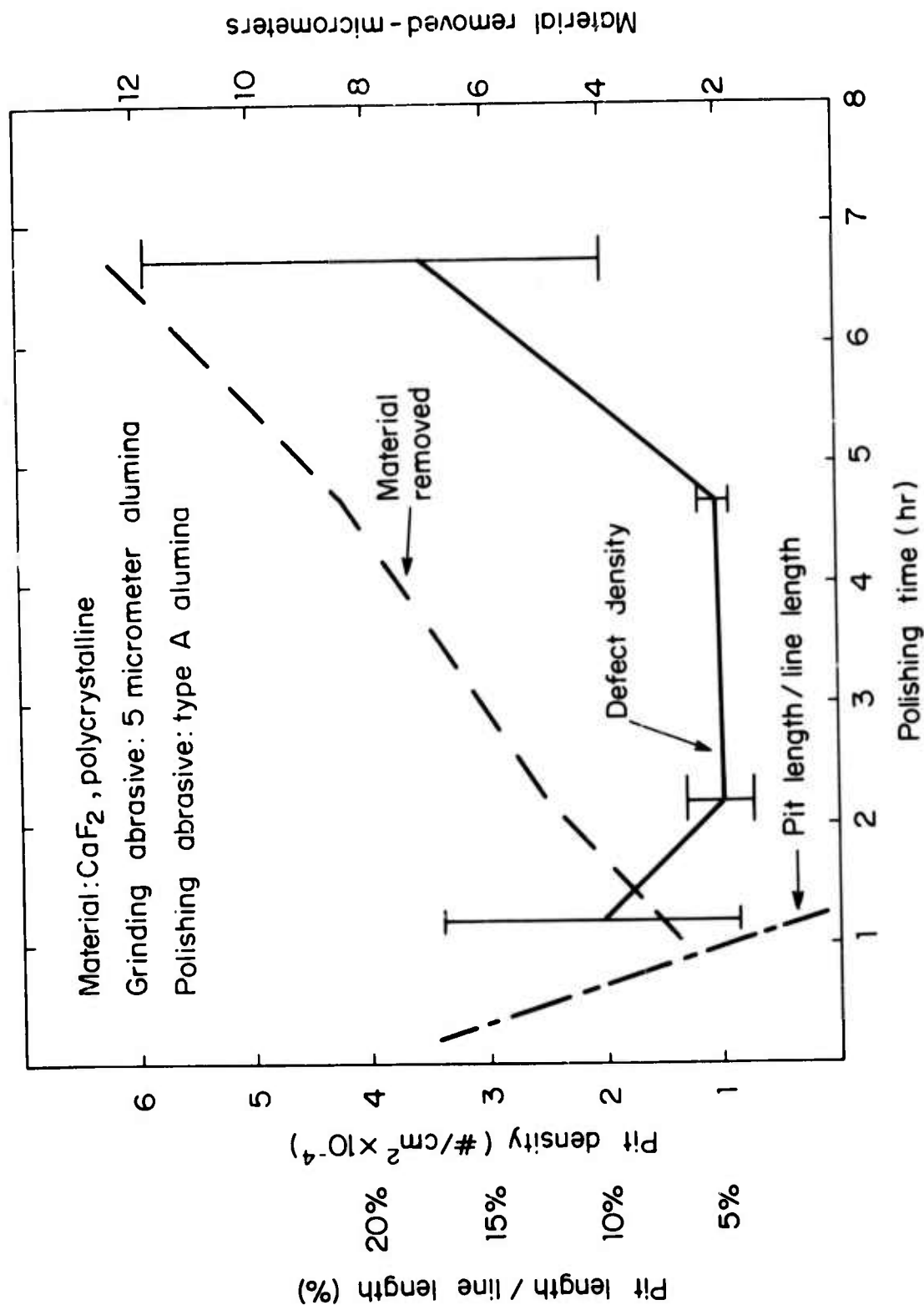


Fig. 3 Surface Defect Density vs Polishing Time and Materials Removal for Ground Polycrystalline Calcium Fluoride Surface Produced by Five-Micrometer Alumina Grinding Abrasives.

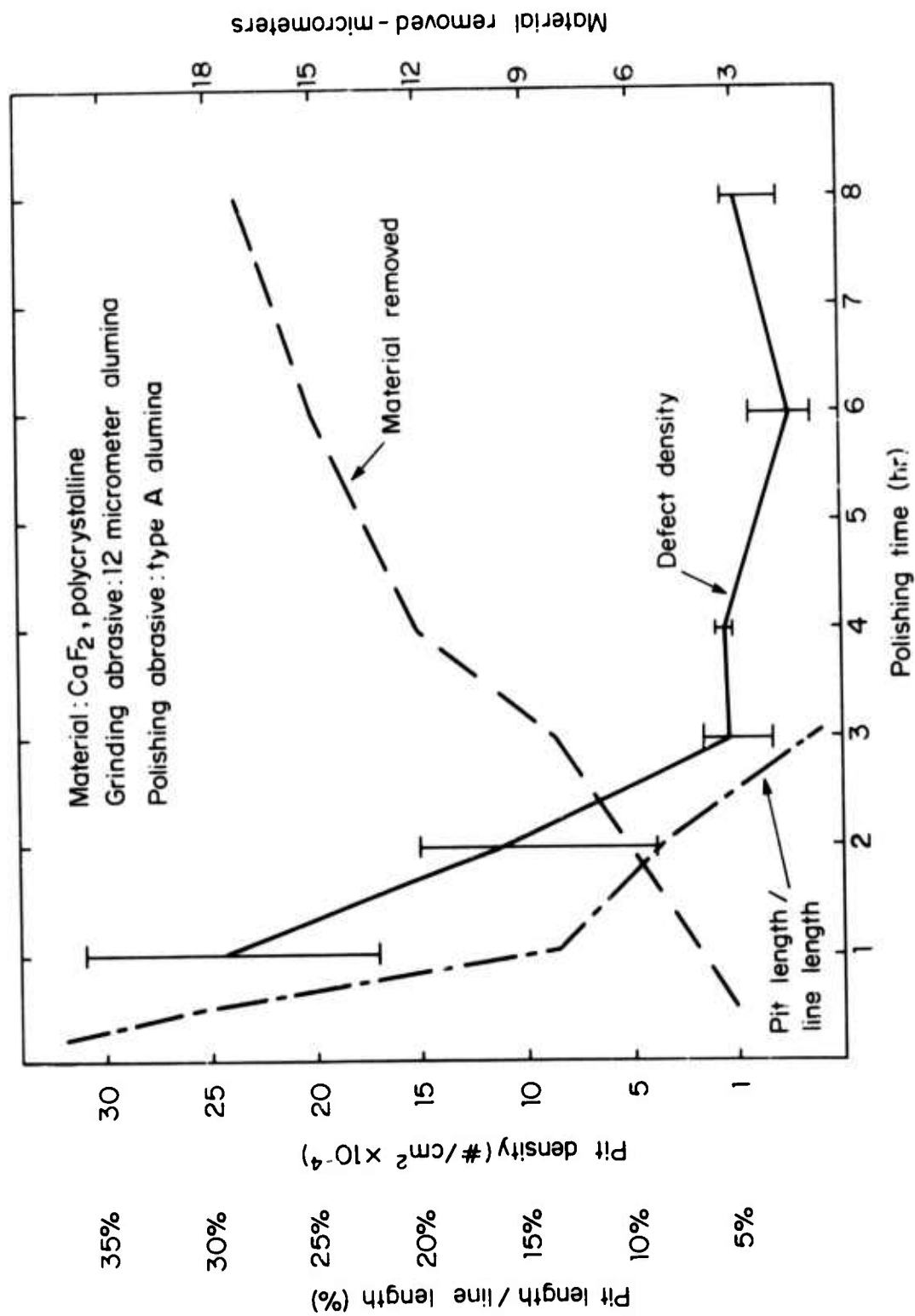


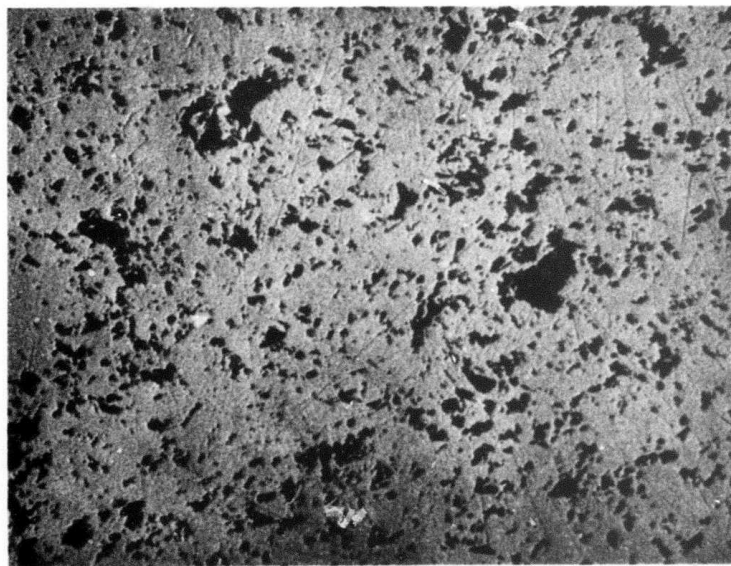
Fig. 4 Surface Defect Density vs Polishing Time and Material Removal for Ground Polycrystalline Calcium Fluoride Surface Produced by Twelve-Micrometer Alumina Grinding Abrasives.

The microstructures presented in Fig. 5 were typical of those produced by the polishing of ground zinc selenide surfaces. In this instance an M-12 (12-micrometer grinding abrasive) surface is being polished with 0.3 micrometer 'A' type alumina. A total of 64 micrometers of selenide was removed during the experiment; this corresponds to five times the grinding compound diameter and is on the order of the selenide grain size. In this case, the surface is nearly developed after 1.75 hours which corresponds to the removal of 12 micrometers (Fig. 5c) and no significant changes occur from 2.75 hours (15 micrometers removed), (Fig. 5d) through 19.25 hours (64 micrometers removed).

Figure 6 summarizes the microstructure analysis taken from the photographs. Error bars on the pit count line correspond to the range of pit counts determined in each set of the three photographs. As in the calcium fluoride case, the surface typical of the polishing abrasive is formed soon after a surface layer comparable to the final grinding abrasive is removed. Scratches on the surface are probably caused by the material which breaks away to form the pits; occasional scratches may be found terminating in pits in most of the photographs in Fig. 5.

That these pits tend to be associated with grain boundaries in the material is shown in Fig. 7 which contains unetched and etched views of the same area of a selenide surface polished with 'A'-alumina. These defects are no more than a micrometer or two deep and have been present at more or less the same density throughout the removal of the total 64 micrometers. It would seem reasonable to associate them with bulk defects already present in the selenide material. Examples of these were presented in the previous semiannual report for this program; they are pits and inclusions which are themselves probably associated with grain boundaries.

Difficulties with the control of deposition parameters during the early production runs occasionally produced very high densities of these defects in the form of optically hazy layers or bands lying normal to the deposition direction within clear, less defective material. A single experimental attempt to correlate such highly defective regions in chemical vapor-deposited zinc selenide with high pit densities on their polished surfaces, however, failed to show any statistically significant correlation. In this experiment, samples

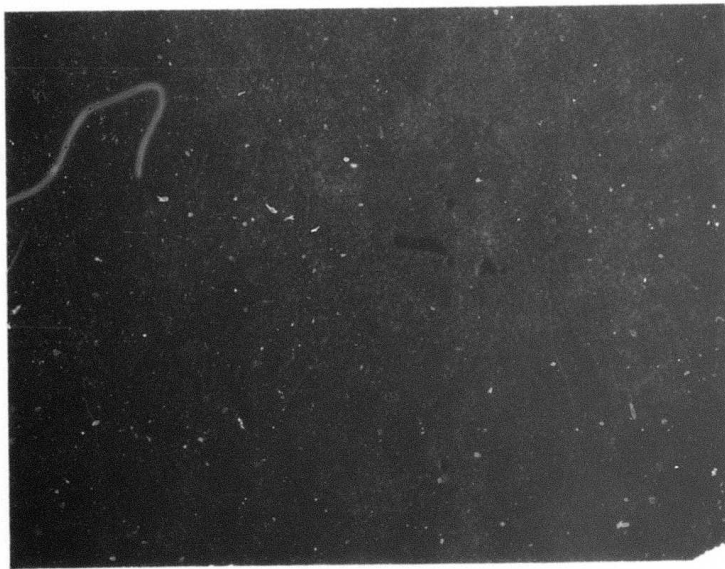


a) After 15 Minutes Polishing, 3 μ m
Removed. 187X



b) After 45 Minutes Polishing, 5 μ m
Removed. 187X

Fig. 5 Microstructures Produced During Polishing of
Ground Polycrystalline Zinc Selenide Surface
Produced by Twelve Micrometer Alumina
Grinding Abrasive.



c) After 1.75 Hours Polishing, 10 μm
Removed. 187X



d) After 2.75 Hours Polishing, 15 μm
Removed. 187X

Fig. 5 (Cont'd)

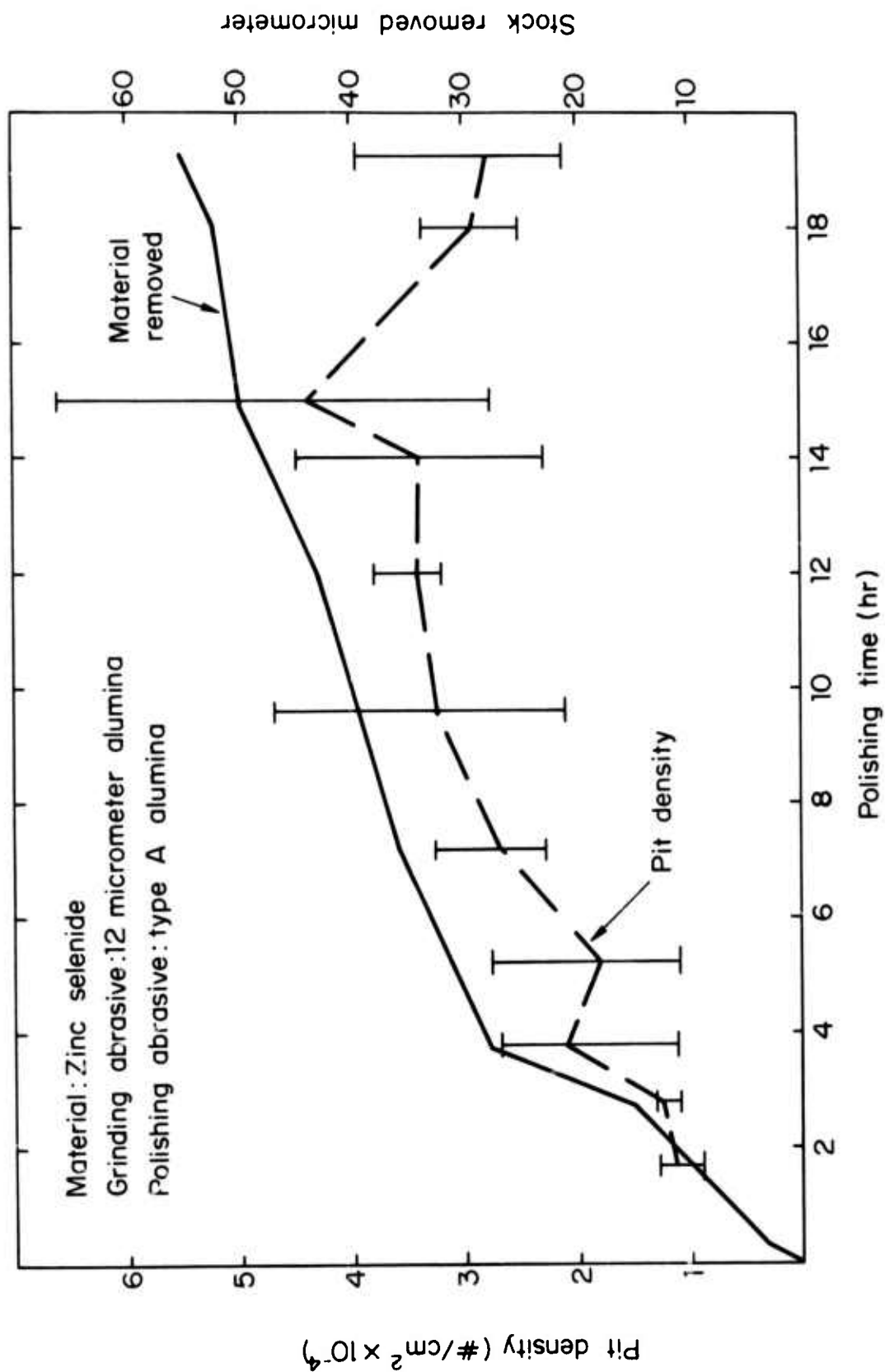


Fig. 6 Surface Defect Density vs Polishing Time and Material Removal for Ground Polycrystalline Zinc Selenide Surface Produced by Twelve-Micrometer Alumina Grinding Abrasive.



50 Microns

a) Unetched Surface



50 Microns

b) Etched Surface

Fig. 7 Polishing Damage on ZnSe. 378×

of zinc selenide cut parallel and normal to the original deposition direction were polished together, surrounding a central piece taken from a run which contained no band.

Surface defect densities were determined on and away from the intersections of these bulk defect bands with the polished surfaces of a transverse section, on the surface of a parallel section, and on the larger central piece. Although the central piece had the lowest average density (defects on five photographs of each were counted to obtain averages), no statistically significant differences among the pieces could be demonstrated. Although there was no marked deterioration of the specimen edges, it is entirely possible that material broken from the edges of the pieces caused further damage at grain boundaries on the surfaces which masked variations caused by the presence or absence of bulk defects. Champfering and polishing the edges of both zinc selenide and calcium fluoride does improve the reproducibility of subsequent conventional polishing steps. Edge polishing (to an 'A' -alumina finish) has been adopted as a standard step in the polishing procedure.

These experiments do demonstrate, however, that cleavage produced in the grinding process did not produce the defects in polished zinc selenide. Cleavage damage would appear within the grains of the microstructure and would probably be sharply reduced by the removal of a surface layer equal in thickness to the grain size. Note that the selenide and fluoride surfaces considered here did not contain any remnant damage from the initial grinding material which is used to produce blanks from the as-deposited materials. Once the depth of damage produced by this operation has been determined, the results obtained here may be used to select reasonable grinding and initial polishing schedules.

2.1.2 Conventional polishing, potassium chloride

Glycerol triacetate (triacetin), a compound first proposed by H. Bennett¹ of the Naval Weapons Laboratory, was used as the slurry medium for potassium chloride polishing. In a preliminary test, a block of potassium chloride single crystals was run for three hours under its own weight on a beeswax lap, submerged in triacetin without abrasive. There was no measurable material removal and scratches on the surface

appeared to be fresh and unetched. The potassium chloride appears to be quite insoluble in triacetin, although there may be a very slight reaction between triacetin and the wax. Triacetin wiped from a pitch lap is discolored by a small quantity of pitch dissolved in it. Beeswax laps run immersed in triacetin bowl-feed polishing experiments have separated from their aluminum backing plates, perhaps because of triacetin attack of the metal-wax interface.

To investigate the efficiency with which triacetin (and remnant beeswax) is removed from potassium chloride, the series of calorimetric absorption measurements summarized in Table 1 was performed on a one-inch square by four-millimeters thick single crystal from Optovac.

Cleaning between the treatments was performed by immersing the sample in ultrasonically agitated isopropanol for 15 seconds, rinsing in isopropanol, immersing the sample in boiling Freon 113 for 30 seconds, and drying it in the Freon vapors.

The calorimeter is sensitive to about one part in 10^4 , so the difference between the etched samples and the one polished without abrasive cannot be considered to be significant. The sample polished with triacetin and alumina appears to be significantly more absorbing, and the effect of using dirty solvents for "cleaning" is apparent. This final surface treatment was also shown to be contaminating by the attenuated total reflection technique discussed below.

In a related set of experiments, the infrared absorption spectrum of triacetin was obtained by attenuated total reflection (ATR) spectroscopy. This experimental apparatus, manufactured by the Harrick Company, sends the sample beam of a Perkin-Elmer Model 457 spectrometer through a sample as shown in Fig. 8. The multiple reflections of the beam accentuate absorptions caused by compounds on the sample surface. The triacetin spectrum, Fig. 9a, was obtained by allowing a one percent solution of triacetin in isopropanol to dry on a potassium chloride ATR plate. Note that several triacetin absorptions occur in the important wavelength range between 9 and 10.6 micrometers. The cleaning procedure described above does appear to clean triacetin from highly polished potassium

TABLE 1
CALORIMETRIC MEASUREMENTS OF
POTASSIUM CHLORIDE CLEANING

<u>Treatment</u>	<u>Fraction Absorbed</u>	<u>Apparent Absorption Coefficient</u>
1. Chemical polish, Concentrated HCl Clean	0.00077	0.00193
2. Hand-held polish Beeswax lap and Triacetin. No abrasive Clean	0.00080	0.00199
3. As step 2, but using Type A-alumina abrasive. Clean	0.00094 - 0.00099	0.00235 - 0.00247
4. Chemical Polish, Concentrated HCl Clean	0.00077	0.00193
5. As step 2, but washing in solvents used for previous washing steps.	0.00137 - 0.00149	0.00342 - 0.00374

ATR SPECIMEN

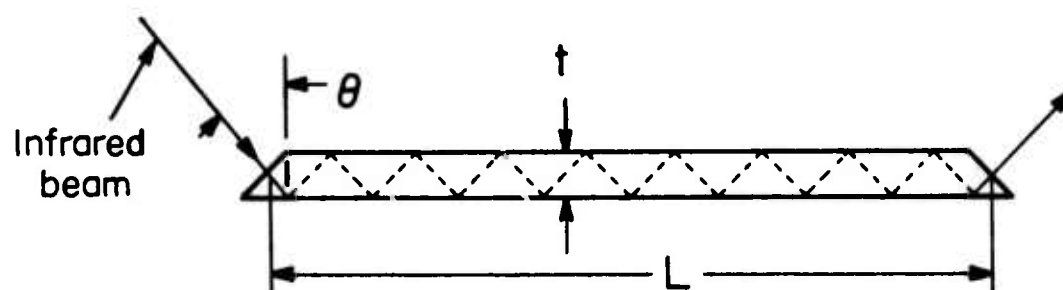


Fig. 8 Attenuated Total Reflection Spectroscopy Sample - Schematic.

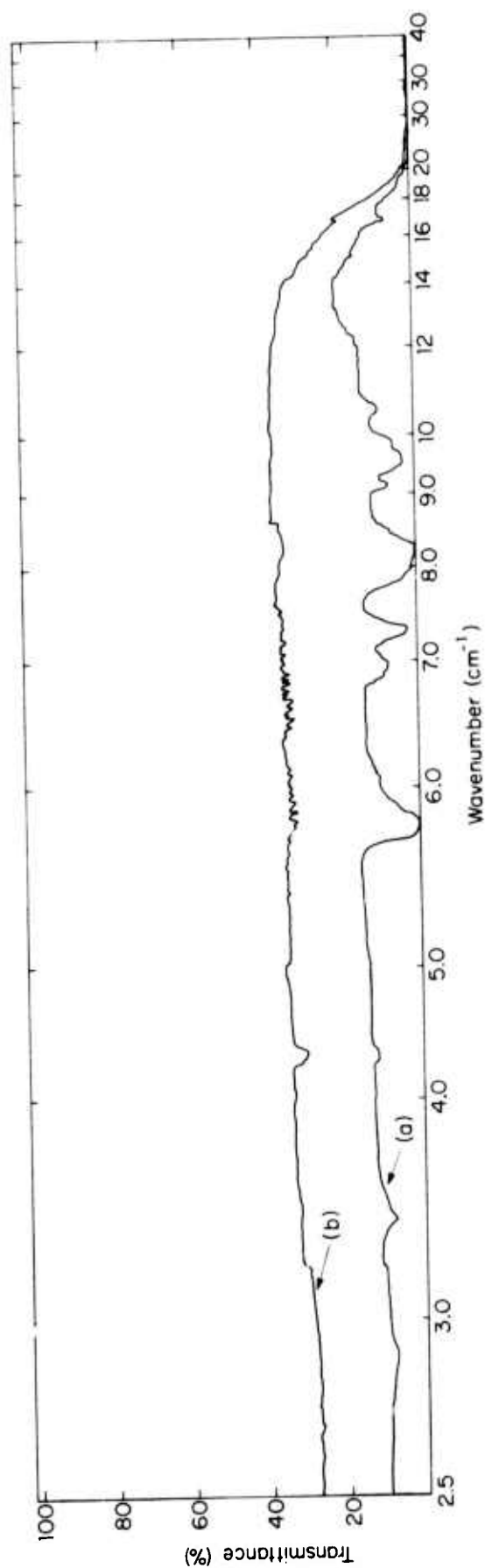


Fig. 9 Attenuated Total Reflection Infrared Spectra of Triacetin-Contaminated and Cleaned Potassium Chloride.

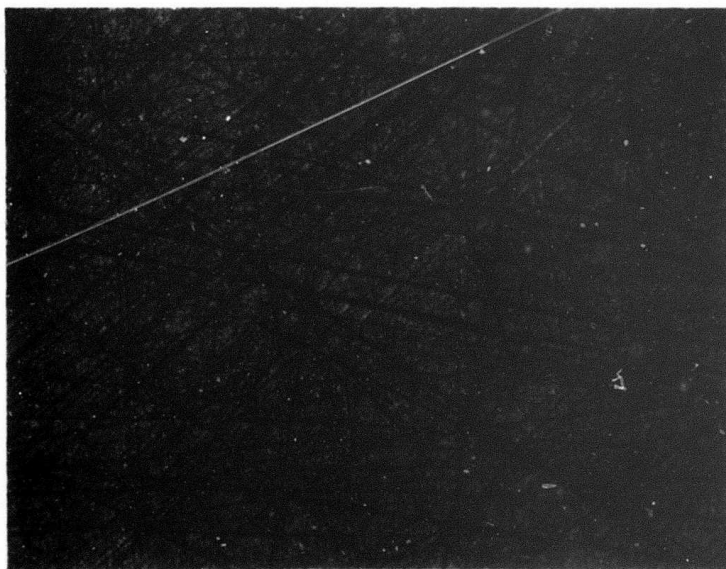
chloride surfaces (Fig. 9b). The absorption at 4.25 and the "noise" between 5 and 7 micrometers are caused by carbon dioxide and water vapor in the laboratory atmosphere.

2.1.3 Bowl-feed polishing

A 4-inch diameter beeswax lap was mounted inside an 8-inch diameter bowl for bowl-feed polishing of potassium chloride specimens using triacetin as the slurry medium. Potassium chloride single crystals conventionally polished with 'A'-alumina (on a beeswax lap using triacetin) were bowl-feed polished in a ten percent by weight suspension of 'B'-type alumina in triacetin. Results are summarized in Fig. 10, where the initial 'A'-surface (Fig. 10a) is seen first to improve (Fig. 10b) and then to degrade with further polishing (Fig. 10c,d). The initial bowl-feed polished surface is the highest quality abrasive polish produced on potassium chloride using wax lap during this project. The deterioration may have been caused by surface contamination introduced when the specimens were inserted in the microscope or by coarse particles in the 'B'-alumina. In Fig. 11, scanning electron micrographs of a 'B'-alumina specimen is compared with a sample of Alon*-fumed alumina which was prepared for inspection by the same technique. The large particle of 'B'-alumina, nearly 70 micrometers across, is an agglomerate of smaller particles. Relatively hard materials would almost certainly break down such large particles to grains more characteristic of the abrasive type and polish accordingly, while soft materials might simply be scratched by the agglomerate particles. Of the alumina abrasives, type 'B' has produced the most variable surfaces on these soft materials.

Itek Corporation² completed their subcontracted study of zinc selenide surface finishing with an evaluation of continuously recycled abrasive polishing. In this technique, the slurry is continuously played onto the lap surface by a pump. The extent to which the coarser abrasive fractions are allowed to settle out of the slurry can be controlled to some extent. The procedure has been used successfully by Itek to polish glass and metal surfaces with abrasives other than alumina, but they found that

* Trademark of Cabot Corporation.

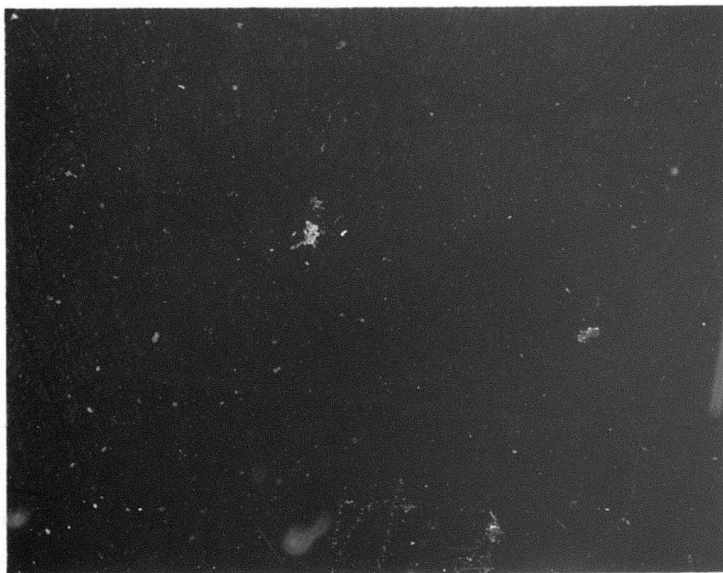


a) Original Surface. 187X



b) After 15 Minutes. 187X

Fig. 10 Potassium Chloride Bowl-Feed Polished in Triacetin Slurry of 'B' - Alumina.

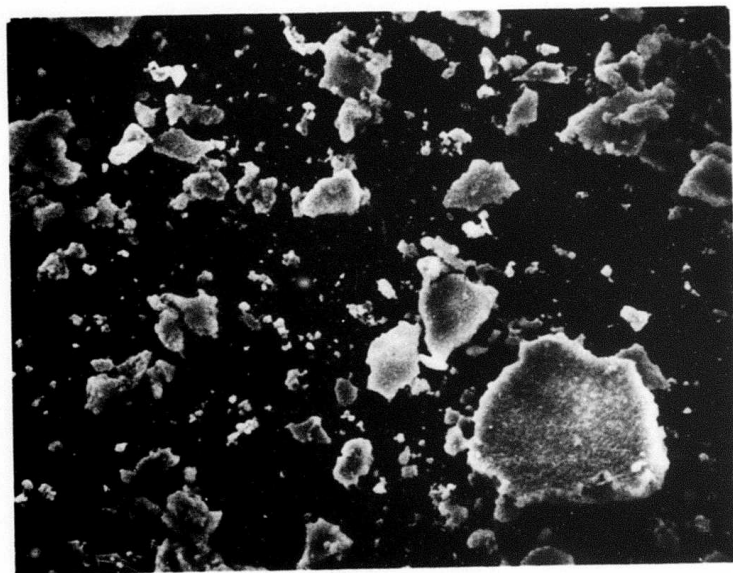


c) After 45 Minutes. 187×

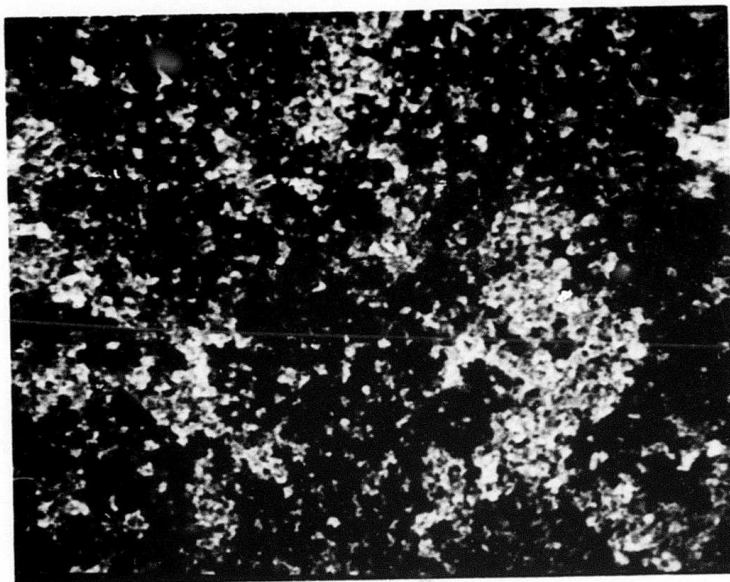


d) After 60 Minutes. 187×

Fig. 10 (Cont'd)



a) Universal Type "B" Alumina. 400X



b) Alon Fumed Alumina. 5000X

Fig. 11 Scanning Electron Micrographs of Alumina Abrasives.

both 'A' - and 'B' -type alumina settled out of suspension too rapidly to produce any significant polishing of the zinc selenide specimens. A wetting agent (Everflow, marketed by Universal Shellac Co.) was used in an attempt to obtain better abrasive suspension, but it degraded the selenide surfaces.

Light scattering from a sample of the bowl-feed polished zinc selenide, produced and evaluated at Itek during the first report period, was measured in the Raytheon scattering apparatus. This sample was polished on a pitch lap which formed the bottom of an 'A' -alumina slurry. It is seen to be intermediate in quality between conventional and bowl-feed 'B' -alumina surfaces (Fig. 12).

In summary, bowl-feed polishing using 'B' -type alumina abrasives has produced the highest quality mechanical polish on all three materials studied in this project. The results of the process are variable and some of the variability may be caused by agglomerated abrasives. Bowl-feed polishing of all three materials using the fumed alumina abrasive illustrated in Fig. 11 is being evaluated.

2.2 Chemical Polishing

2.2.1 Potassium chloride

Of the materials being studied for use as high power laser windows, none would benefit more from the development of chemical polishing procedures than potassium chloride. Although abrasive polishing techniques for the material are improving, it is reasonable to expect that surfaces produced by abrasive polishing will contain both scratches and embedded abrasive material, which at present is most likely to be alumina. Concentrated hydrochloric acid has been shown to be an effective chemical polish for single crystalline material³ and has more recently been used to polish polycrystalline material.⁴ In this case, however, the individual grains, comprising the whole etch at different rates, produce a stepped surface, the development of which has not been studied in detail. Further, chemical polishing of large area optical elements by immersion while preserving their optical figures is likely to be a difficult task.

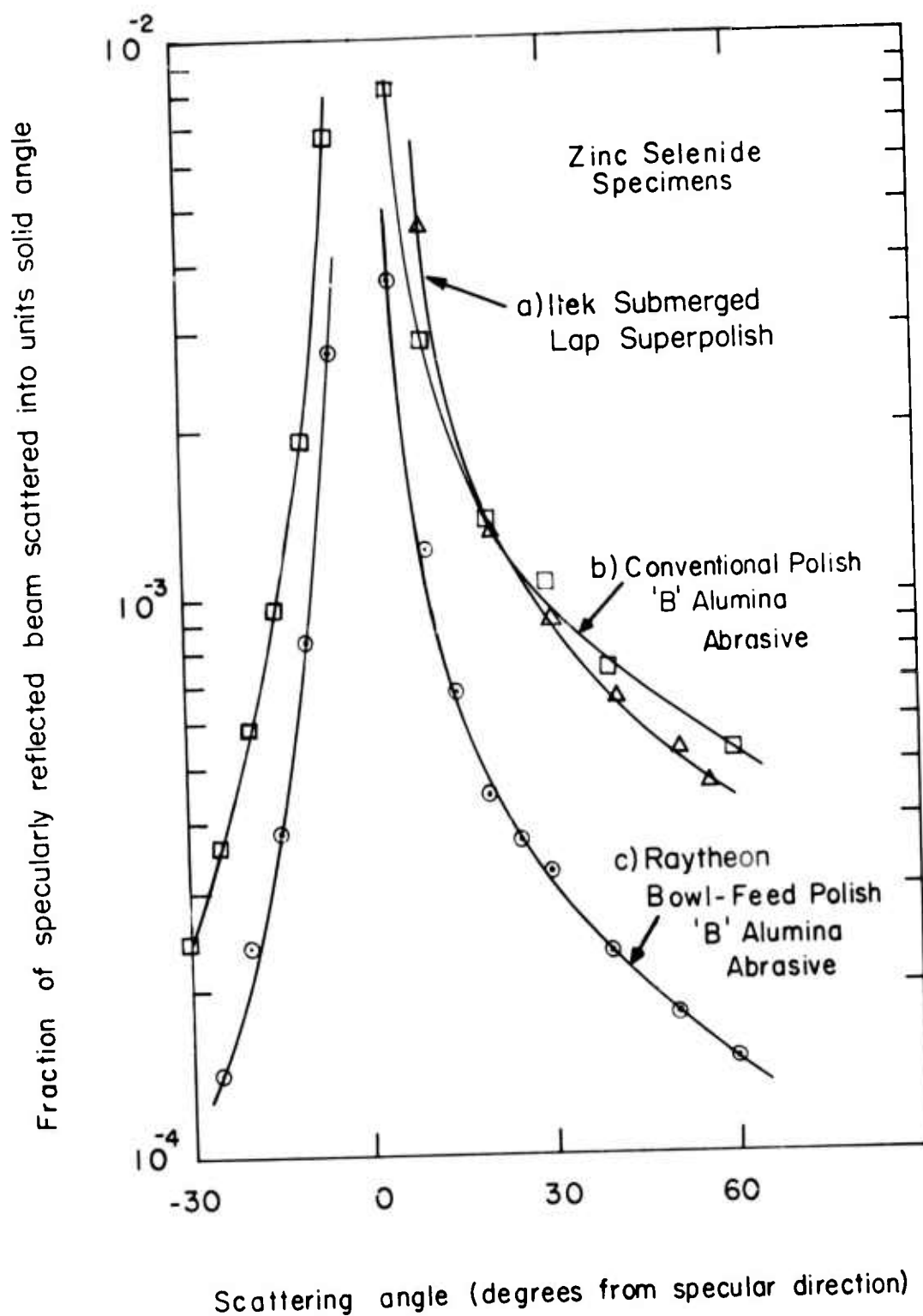


Fig. 12 Light Scattered into Unit Solid Angle vs Scattering Angle - Selenide Samples.

Since the most damage-resistant surfaces reported for potassium chloride have been produced by hydrochloric acid etching⁴, however, techniques which are capable of acid-polishing large polycrystalline potassium chloride optical elements should be developed.

The essential requirements of the etch are that it remove surface damage and surface material at a controllable rate, that the rate does not depend too strongly on crystalline orientation, and that the etching action may be stopped and the etchant removed from the surface uniformly and completely. These characteristics of hydrochloric acid and related etchants are being evaluated in a series of experiments begun at Raytheon during this second report period. Etch rates are being determined by etching and weighing samples of known weight and area. The variation of etch rate with orientation is being determined by tracing etched polycrystalline surfaces with a Dektak^{*} profilometer. Other examples of this approach to polycrystalline surface evaluation are given in Sec. 2.4. Surface cleaning efficiency may be determined by calorimetric absorption measurements and microscopic examination, and optical quality by figure and scattering measurements.

In experiments performed to date, the etch rates of single and polycrystalline potassium chloride in concentrated hydrochloric acid and of polycrystalline potassium chloride in a 1:1 mixture of hydrochloric acid and triacetin have been determined. Results are summarized in Table 2.

TABLE 2
ETCH RATES DETERMINED FOR POTASSIUM CHLORIDE MATERIALS

<u>Material</u>	<u>Etchant</u>	<u>Rate (micrometers/ minute)</u>	<u>Remarks</u>
Pure KCl Single Crystal	HCl	11.5 ± 0.7	Clean surfaces
Polycrystal KCl: 200 ppm Sr	HCl	7.8 ± 0.9	Clean surfaces
Pure KCl single crystal	HCl:Triacetin 1:1	~ 0.8	Surface incom- pletely cleaned

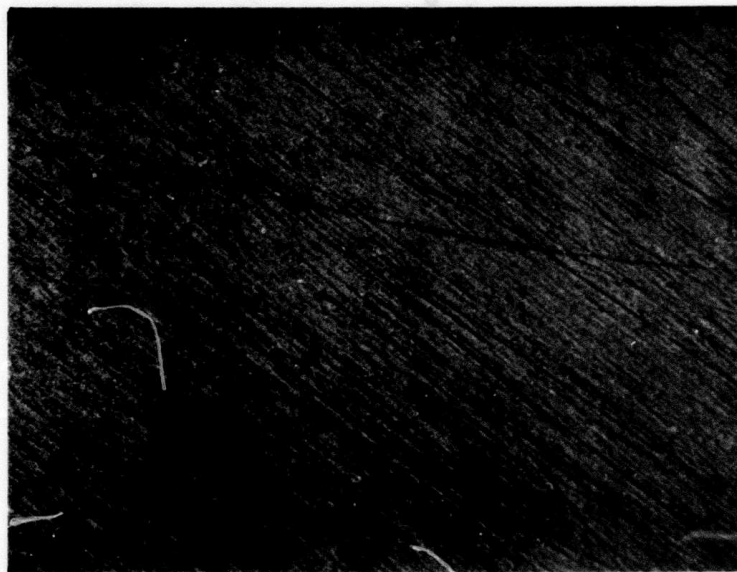
Etching was performed by agitating the specimen in a beaker of etchant, stopping the process in isopropanol, and rinsing in isopropanol and in Freon.

^{*} Trademark, Sloan Technology Corporation.

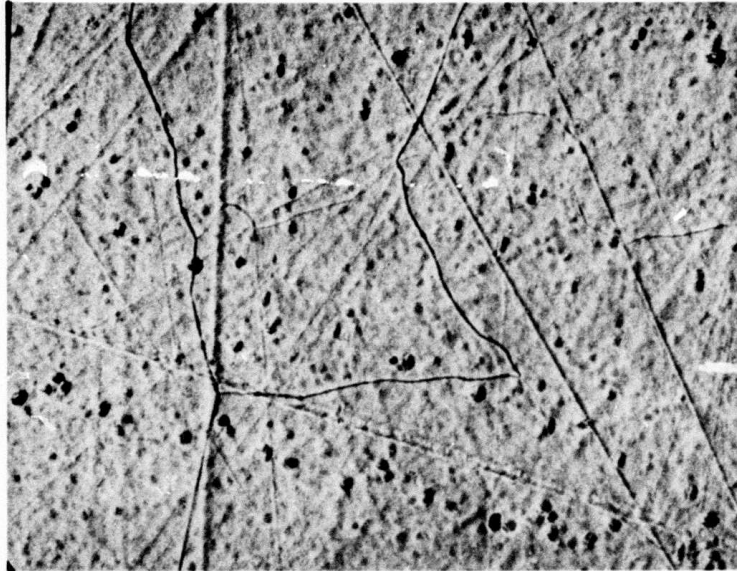
Concentrated hydrochloric acid is seen to remove material at rates on the order of ten micrometers per minute - one wavelength of 10.6 μm radiation per minute - from both the single and polycrystalline material. The difference in rate between the two materials is significant, each rate determination is the average of at least ten measurements made on two similar samples; but whether the difference is due to the strontium doping of the polycrystalline material or to the presence of the variety of grain orientations within it has not been determined. Development of the surface of the polycrystalline specimen is presented in Fig. 13. In this case, the abrasive polish was essentially removed in 90 seconds during which time an average of 11.7 μm of material were removed. This specimen was polished by hand under only its own weight and probably contains as little subsurface damage as any mechanically polished potassium chloride. Grain boundaries, subgrain boundaries, and orientation-dependent surface texture can be seen on the etched surfaces.

Chemical polishing of calcium fluoride and of zinc selenide is carried out on surfaces which are not only superficially more perfect than the original surface used in this experiment, but also freer of subsurface damage which could extend the appearance of surface scratches beyond the removal of the original surface. As a result, dramatic surface improvement is produced on zinc selenide and calcium fluoride by the removal of a micrometer or less of material. For potassium chloride, we must determine the relative contributions of initial surface roughness and subsurface damage to the roughness of lightly etched surfaces. To the extent that the initial surface roughness is the major contributor, an improved mechanical technique would require the etching of less material and could probably be alternated with chemical polishing to produce a surface which is both optically figured and damage-free.

A profilometer trace made of the etched surface in Fig. 13 demonstrated that the surface steps at grain boundaries were on the order of only 500 angstroms high. Such steps would have no effect on the quality of optical elements used for 10.6-micrometer radiation. Note, however, that the first micrometer or so (corresponding to the total material removed by other chemical polishing processes) is removed by hydrochloric acid in

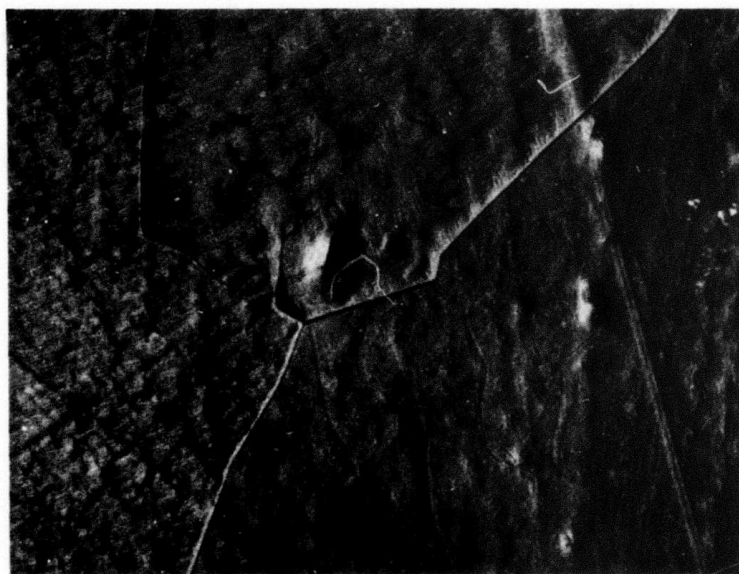


a) Prior to Etch.

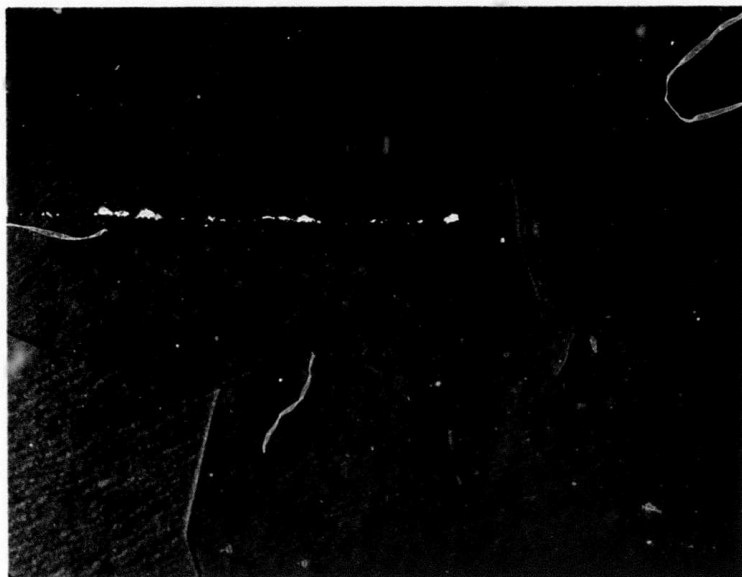


b) After 30 Seconds, $\sim 4.5 \mu\text{m}$
Removed.

Fig. 13 Development of Etched Polycrystalline Potassium
Chloride Surface - Concentrated Hydrochloric Acid
Etch. 187X



c) After 60 Seconds, $\sim 9 \mu\text{m}$ Removed.



d) After 90 Seconds, $\sim 13 \mu\text{m}$ Removed.

Fig. 13 (Cont'd)

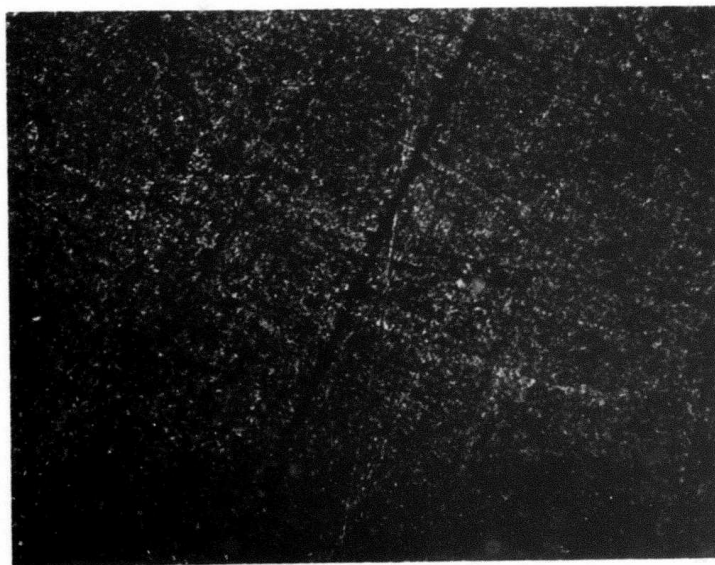
approximately six seconds. This rate of removal is probably too high to permit controlled etching of large optical elements; an etch which operates more slowly than concentrated hydrochloric acid would be most useful. The 1:1 triacetin: hydrochloric acid solution reported in Table 2 is a preliminary attempt to develop such an etch. In this case the etch rate was decreased by more than an order of magnitude below that for pure hydrochloric acid, but the surface quality produced by the etch was significantly poorer. Typical surfaces produced by the triacetate-acid mixture are summarized in Fig. 14. Note that deep scratch remnants persist after 10.5 minutes etching ($8.4\mu\text{m}$ material removed, Fig. 14d).

In a parallel series of experiments, weaker solutions of hydrochloric acid in triacetin were used as chemical-mechanical polishing agents. Potassium chloride samples were run on beeswax laps immersed in triacetin containing up to five percent hydrochloric acid for times as long as two hours. No measurable surface improvements or material removal was produced.

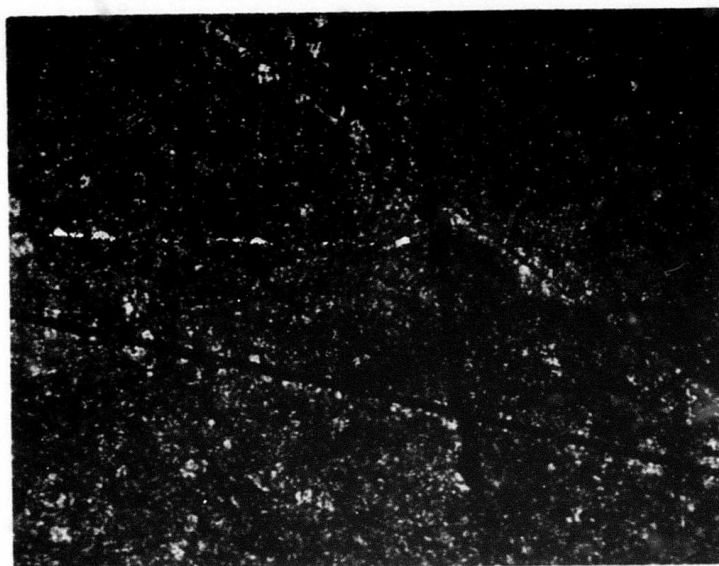
Efforts to identify an etch for potassium chloride which will produce the high surface quality obtained with hydrochloric acid but at a slower rate are continuing. Both immersion etches and solution to be used along with polishing laps are being considered.

2.2.2 Zinc selenide

During the first report period, solutions of bromine in methanol were used to chemically polish zinc selenide. The surfaces produced by the technique depended critically upon the concentration of the solution and the method of addition of the solution to the lap and were not consistent in quality. Further, the alcohol solution cannot be used in conjunction with pitch laps. In this report period, a series of aqueous solutions of oxidizing agents was evaluated. The ferricyanide etch first reported by Hughes Research Labs was used to rank prospective polishing lap materials, and variations of the ferricyanide etch concentration were studied.

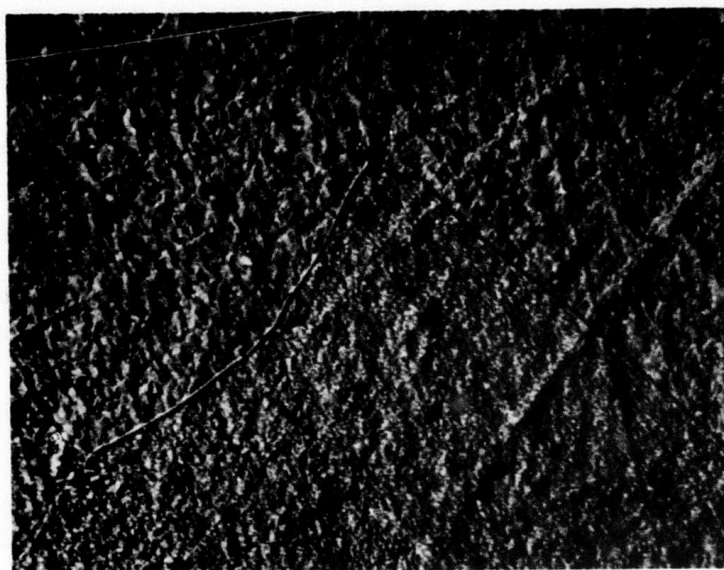


a) Prior to Etch



b) After 30 Seconds Etch -
No significant material removed

Fig. 14 Development of Etched Polycrystalline Potassium
Chloride Surface - Hydrochloric Acid: Triacetin (1:1)
Etch, 187X



c) After 330 Seconds Etch - $\sim 5 \mu\text{m}$
Removed

Fig. 14 (Cont'd)

Solutions listed in Table 3 were used to chemically polish zinc selenide with the results indicated. Blocks containing three 1.5-inch diameter zinc selenide discs were run on Politex* "Supreme" polishing pads saturated with the solutions. Etching was stopped by flooding the rotating lap surface with deionized, filtered water. Itek Corporation, working with the ferricyanide etch, adopted the procedure of quickly removing the etched work piece to a clean, water-flooded lap. Either approach can be used, but the former seems more convenient.

In general, any solution capable of oxidizing the selenium ion to some higher valence state should affect some etching of the material. Two of the solutions listed, potassium permanganate and potassium dichromate, should be capable of oxidizing the selenium to a relatively soluble selenite or selenate. They were selected in the hope that they would etch the material without producing an insoluble reaction product. Weaker oxidizing agents should produce an insoluble selenium layer. In fact, all reagents produced reaction layers. The permanganate did oxidize the selenium completely but was itself reduced to manganese dioxide which adhered to the selenide surface. The dichromate solution produced an unidentified reaction product. Sodium hypochlorite solution produced a pitted surface and attacked a pitch surface on which it was used. Although further work with dichromate solutions might produce a usable chemical polish for zinc selenide, it seems more reasonable to optimize the use of the ferricyanide etch.

TABLE 3
OXIDIZING AGENTS FOR CHEMICAL POLISHING ZINC SELENIDE

<u>Compound</u>	<u>pH</u>	<u>Concentration</u>	<u>Comments</u>
Potassium Permanganate	acidic	Saturated Solution	Adherent MnO ₂ , Poor polish
Potassium Dichromate	acidic	Saturated Solution	Unidentified, forms slowly, usable as polish
Potassium Ferricyanide	alkaline	1 molar	Residue not adherent, usable as polish
Sodium Hypochlorite	alkaline	5 percent	Surface pitting, adherent residue, attacks pitch lap

* Trademark, Geoscience Corporation.

Three lap surfaces, Pellon PAN W^{*}, Pellon XP-500^{*}, and Politex "Supreme"^{**} were used to polish zinc selenide samples with a 1:1 dilution of the ferricyanide etch.

Approximately one pound per square inch pressure was applied to the samples which were polished for fifteen minutes with each pad. Results are summarized in Fig. 15. The most scratch-free surface was produced by the Politex pad (Fig. 15a); the PAN W pad left rather more scratches on the surface and, in areas close to the edge, did not completely remove the reaction product. Pellon XP-500 is a very soft, highly porous material which, in this case, polished only the specimen edges (Fig. 15c,d). Etchant solution was apparently squeezed from the soft material by the workpieces.

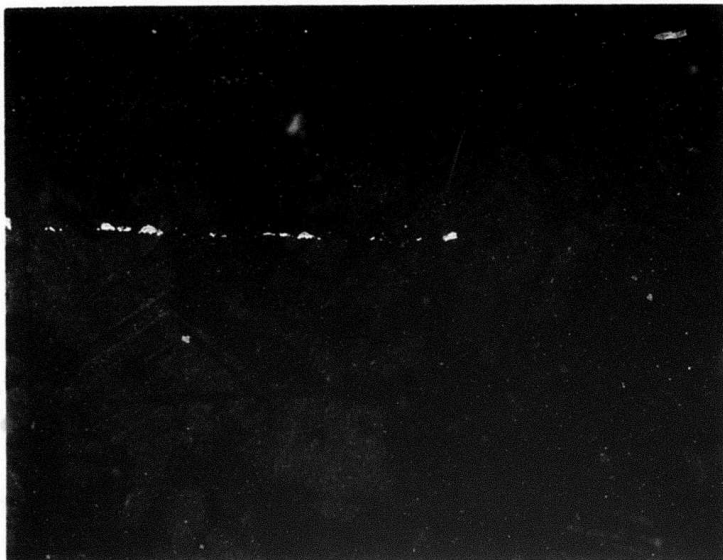
The ferricyanide etch used by Hughes Research Laboratories is an alkaline, approximately one-molar solution. Used on a pitch lap for two minutes, it removes remnant scratches and produces some grain relief. Itek Corporation² experienced some difficulty in stopping the etch uniformly and, as already noted, began removing the workpiece to a second water-flooded lap. Since this procedure might prove difficult to manage with large pieces, various dilutions of the etch were used to slow and control its action. Samples were polished on Politex pads under the conditions discussed above for the polishing surface evaluation. Etchant was added by hand at a rate which maintained a thin layer of solution on the lap. A typical surface generated in the study is presented in Figs. 15e,f. This one was produced using a 5:1 dilution of the etch and polishing for 15 minutes. Although no scattering measurements were made on the surfaces, a 10:1 dilution produced a qualitatively similar surface after 30 minutes' polishing; and a 20:1 dilution produced a somewhat more highly scratched surface in 60 minutes. More extended polishing with the 20:1 dilution would probably have improved the surface. The 5:1 dilution/ 15 minute polishing procedure appears to be a reasonable compromise between speed of operation and vigor of etch; and it has been

* Pellon Corporation

** Trademark, Calscience Corporation



a) Politex "Supreme" Pad

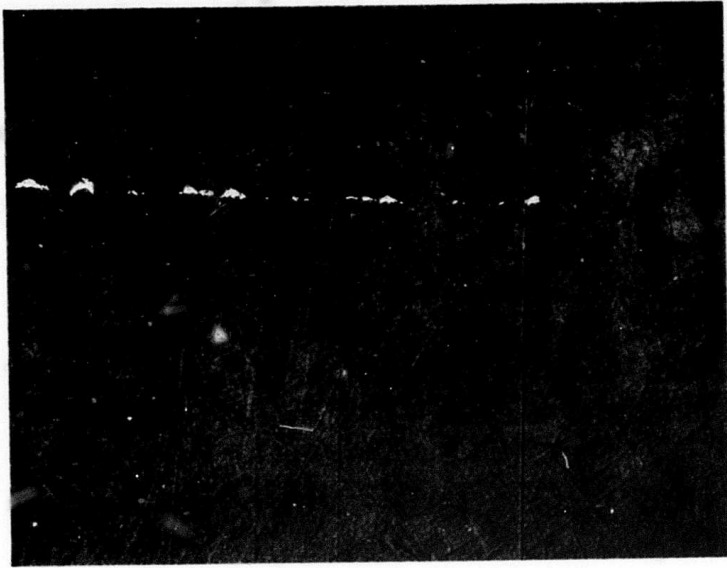


b) Pellon Pan-W Pad

Fig. 15 Chemically Polished Zinc Selenide Surfaces Produced by Various Lap Surfaces. 187X

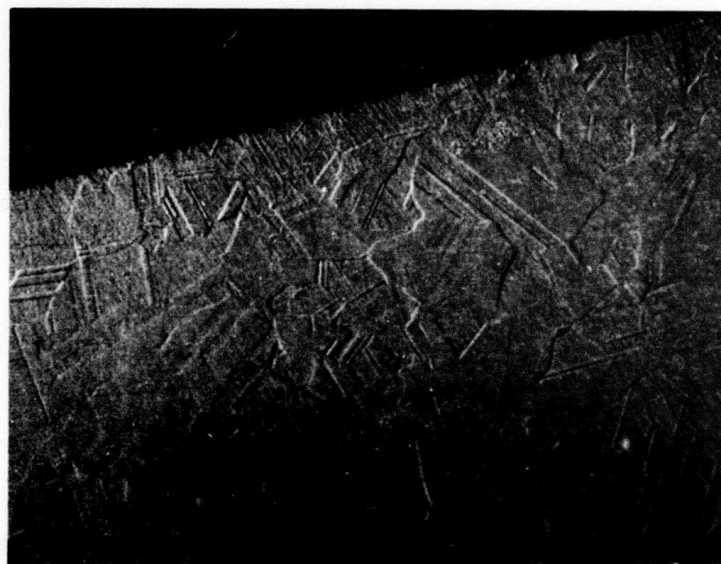


c) Pellon XP-500 Pad, Edge Area, 187 \times



d) Pellon XP-500 Pad, Center Area,
187 \times

Fig. 15 (Cont'd)



e) Edge Area, Optimized Procedure



f) Center Area, Optimized Procedure.

Fig. 15 (Cont'd)

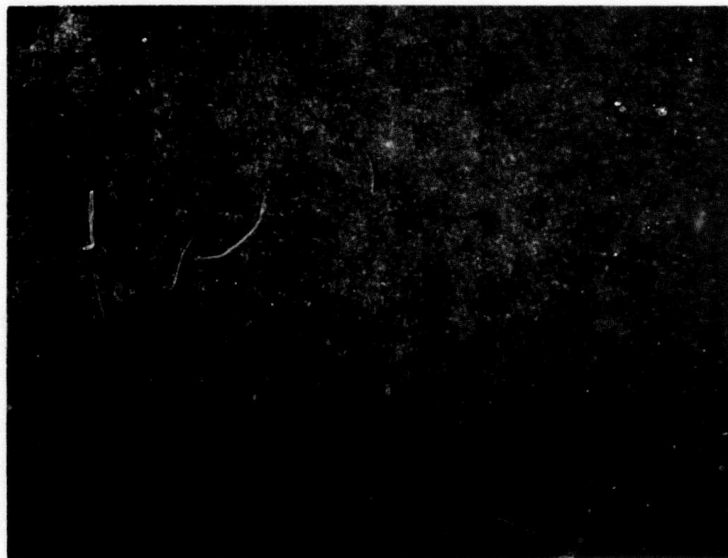
included in our standard sequence. The surfaces of these chemically polished specimens commonly have a higher density of remnant scratches at the edge than in the central portion. This is probably a reflection of the increased subsurface damage produced at the specimen edge during polishing. It should serve to demonstrate that the results of the chemical etching procedure may be variable at least to the extent that the preliminary abrasive steps are variable.

2.2.3 Calcium fluoride

Calcium fluoride surfaces which are very nearly defect-free to the Nomarski microscope may be prepared by conventional abrasive techniques and improved by bowl-feed polishing. Further, the alumina abrasive used to produce these surfaces is essentially transparent to radiation for which high power fluoride optics might be used. In this case, the important function for a chemical polish to perform is the removal of surface defects which might otherwise act as extrinsic damage sites. Brewster window configurations which permit the use of uncoated fluoride optics may be used for some applications. In such cases, chemical polishing could be used to clean and recondition used windows.

A one-molar aqueous solution of ammonium chloride was used as a chemical-mechanical polish for single and polycrystalline calcium fluoride. Polishing was done on a pitch lap immersed in the solution. A parallel attempt to determine an etch rate by the etching and weighing technique described for potassium chloride did not produce any measurable weight loss; it appears that in this case an insoluble reaction product is formed which must be removed by the action of the lap.

Microstructures produced by an ammonium chloride etch-polish of polycrystalline material are summarized in Fig. 16. One hour of polishing substantially improves the original rather poorly polished 'A'-alumina surface. Some grain relief is produced and the extent of the scratch removal may be seen to depend upon the grain orientation. Con-

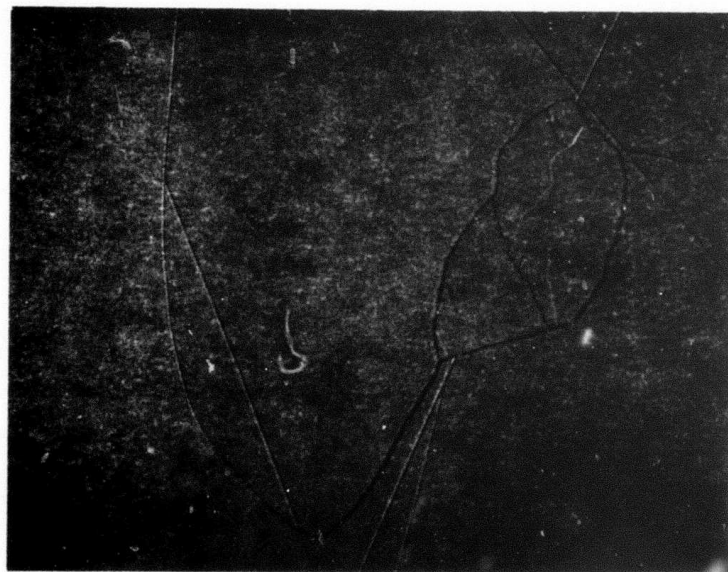


a) Original Surface.

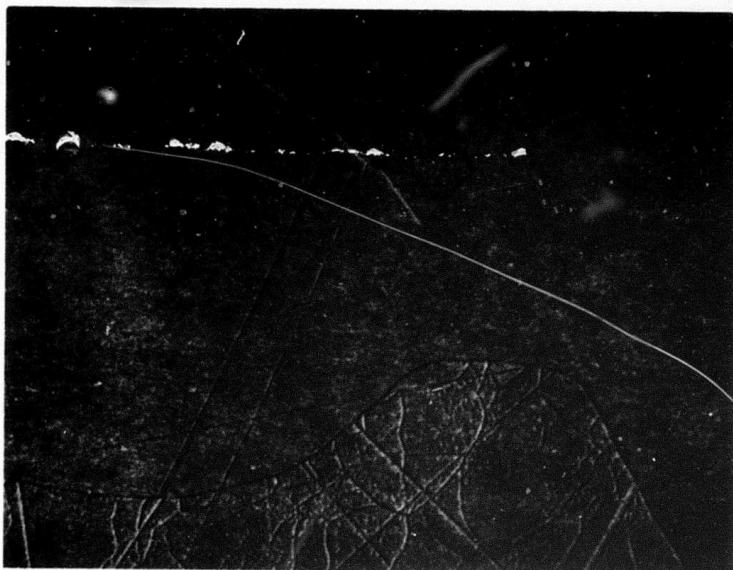


b) After One Hour

Fig. 16
Microstructures Produced by Chemical Polishing of
Polycrystalline Calcium Fluoride - Ammonium Chloride
Etch. 187x



c) After 2.5 Hours, Note Deep Scratches and Grain Boundaries.



d) After 2.5 Hours, Note Subgrain Boundaries and Surface Pitting.

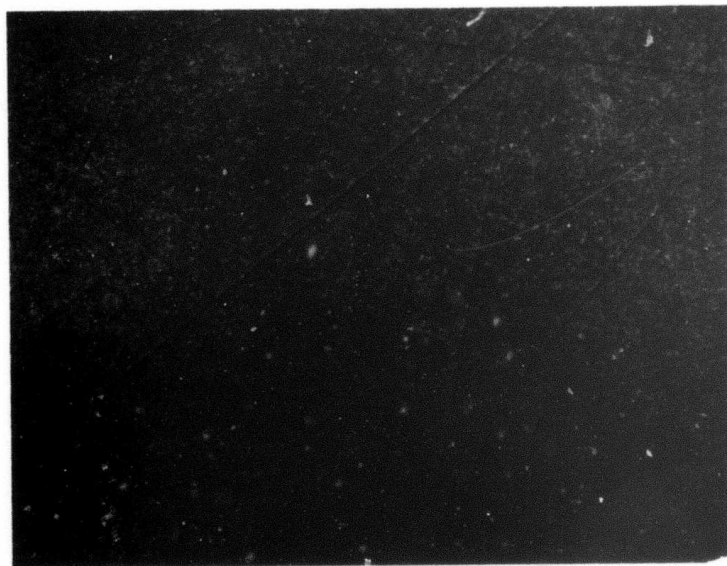
Figure 16 (Cont'd)

tinuation of the procedure for a total of two and a half hours removes all but the deepest scratches (Fig. 16c), but it accentuates the grain boundaries and causes pitting on one grain orientation. In a parallel experiment, a block of six single crystal slices was polished for two hours in the chloride solution. Three of the slices were oriented approximately five degrees from the (100) plane; the other three were a "random" orientation - not close to any simple crystal plane. The "random" slices polished to a surface which was defect-free in the Nomarski microscope while the near (100) slices retained some scratches (Fig. 17).

Highly perfect surfaces are produced on some fluoride orientations by this technique and attempts to improve it are in progress. The effect of concentration and pH will be determined. Since the process appears to depend upon the removal of some insoluble reaction product layer, the effect of trace additions of a fine abrasive such as fumed alumina (Fig. 11b) will be determined. Abrasive additions could be especially useful in conjunction with basic solutions which should produce a surface hydroxide layer.

2.3 Ion-Beam Polishing

Most high power laser windows will require thin film antireflection coatings. It is common practice to heat substrates during thin film deposition in order to improve the adherence and in some cases various microstructural features of the film, such as grain size and porosity. Substrate heating in many cases is primarily a surface cleaning procedure which removes adsorbed moisture and other contaminants. Ion-beam polishing, which actually removes surface layers of the substrate material itself, may, in principle, be used in the deposition with or without additional substrate heating to remove surface contaminants and other surface defects. The process might be particularly useful for final cleaning of large alkali halide windows which, because of their high thermal expansion coefficients and low infrared absorption coefficients, will be difficult to heat uniformly in vacuum. Further, the mechanical properties of halide alloy windows may be adversely affected by typical substrate heating cycles. A full exploration of the utility of ion-beam polishing must include a film deposition task. In this project, the development of surface microstructure is being studied.



a) Near (100) Surface Orientation
Scratches are Probably Exposed
Subsurface Damage. 378X



b) "Random" Surface Orientation
Defect is a Remnant of Abrasive
Polishing. 378X

Fig. 17

Microstructures Produced by Chemical Polishing of Single
Crystal Calcium Fluoride - Ammonium Chloride Etch;
Polishing Time, 2.5 Hours.

During the first report period, ion-beam polishing was also considered as a primary polishing technique, but was shown to produce grain relief on surfaces of polycrystalline specimens of all three materials. The relief is produced by a dependence of the etch rates upon the orientation of the crystallite being etched. As ion milling is continued, initially flat surfaces are progressively transformed into surfaces containing increasingly large vertical steps. Figure 18 is the surface profile, taken with a Dektak^{*} profilometer, of the 60-degree incidence, ion-milled zinc selenide specimen described in the previous report. Note that several sets of surface heights are repeated. As already noted, the etching rate is dependent upon the orientation of the crystal being etched with respect to the ion beam. Repetitions of surface heights reflect repetitions of the total amount of material removed and therefore of crystalline orientations. These repetitions occur frequently in polycrystalline zinc selenide samples because their larger grains commonly contain many twins.

Since the rate at which this surface roughening was produced as a function of the total average material removal and the effect of the material removal on the optical properties of the surfaces could not be determined, a second series of ion-milling experiments has been performed. The ion milling was performed in a Veeco "Microetch" apparatus recently installed at the Research Division. This apparatus is a diffusion-pumped vacuum system in which a three-inch diameter neutralized argon ion beam is directed, as shown schematically in Fig. 19a, onto a sample holder which can be tilted with respect to the argon ion beam and rotated about an axis normal to its surface. In these experiments, an accelerating potential of 500 volts and beam current 11 milliamperes were employed. To minimize sample heating, the sample surfaces were etched for two-minute periods (which corresponded to one sample rotation) separated by three-minute cooling periods. To minimize grain-to-grain relief in the etched surfaces, the ion beam was incident at 84 degrees from the sample normal

Polycrystalline 1.5-inch diameter discs of chemical vapor deposited zinc selenide and hot pressed calcium fluoride (Irtran 3) were etched in separate experiments. Both were bowl-feed polished to nearly scratch-free

* Trademark, Sloan Technology Corporation.

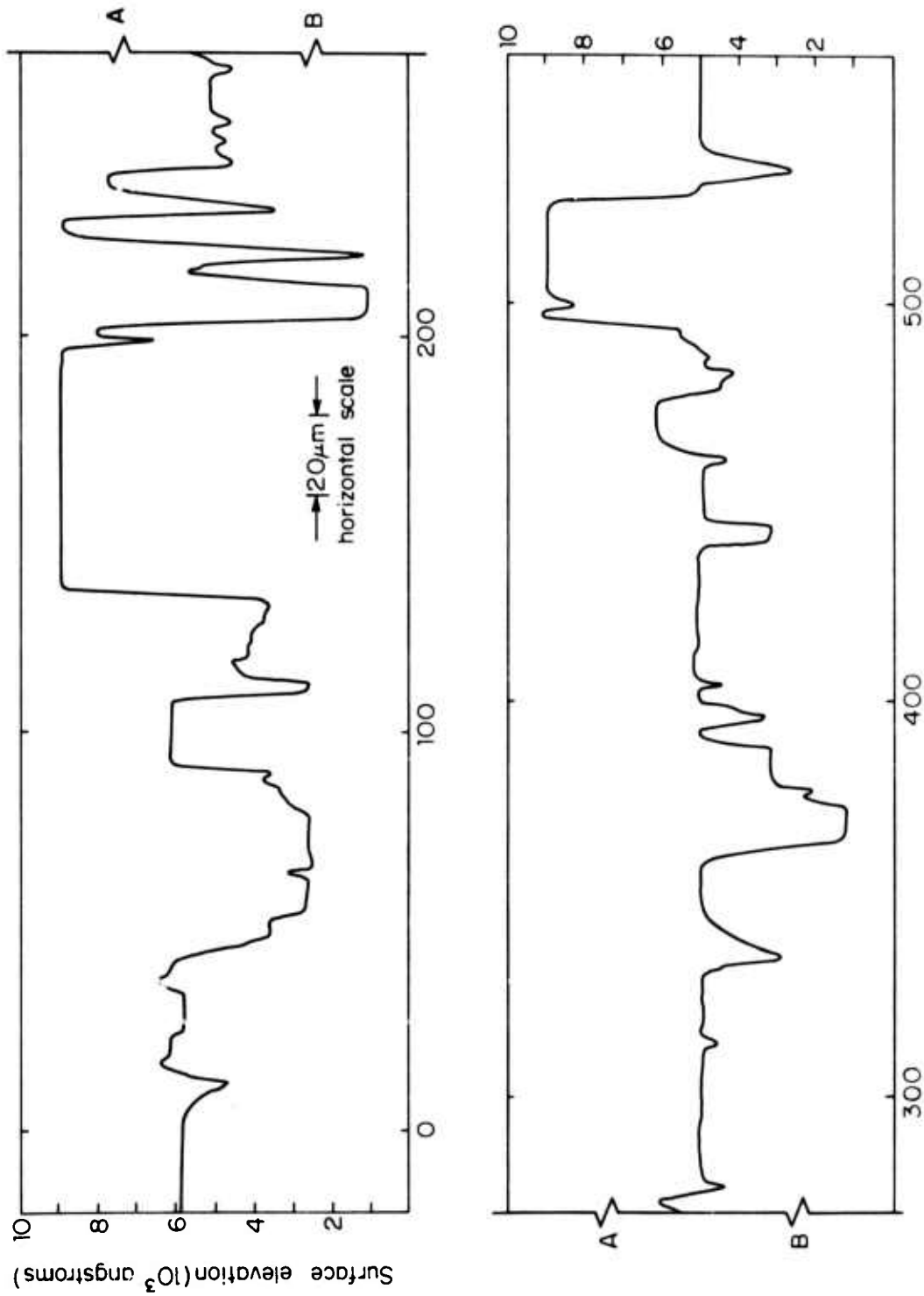
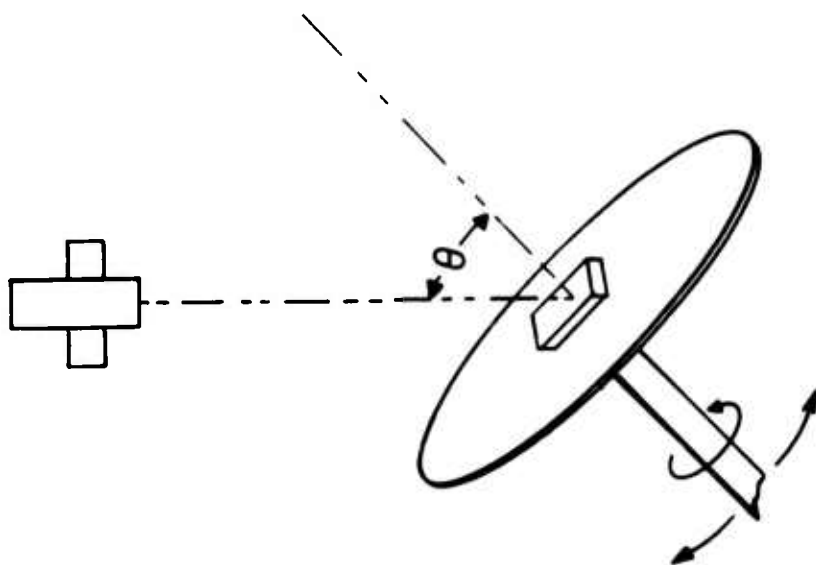
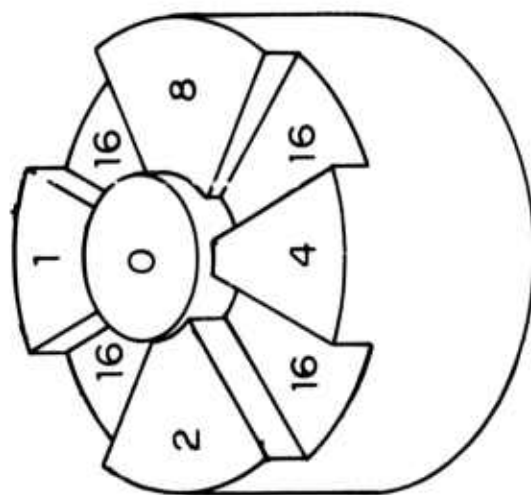


Fig. 18 Surface Profilometer Trace of Ion Beam Polished Zinc Selenide.



c) Veeco unit



b) Polished specimen
(numbers represent
relative etching times)

Fig. 19 Ion Beam Polishing Apparatus and Etched Sample - Schematic.

surfaces prior to the etching. The central portions of the specimen discs were coated with photoresist prior to the etching to provide an unetched reference plane. Etching was then interrupted periodically during the experiment, and each time an additional area on the surface was protected by photoresist. A typical sample produced by the procedure is sketched in Fig. 19b. The material removal and grain relief on the sample were measured with a profilometer, and scattering measurements were made on the zinc selenide specimen. The apparatus used for the scattering measurements was described in the first semiannual report for this project. Since the surface of the calcium fluoride specimen contained some flaws (produced by bulk defects) which would have contributed to the intensity of light scattered from the surface, no scattering measurements were made on it.

Results of the profilometer measurements made on the two samples are summarized in Table 4. The surface reliefs reported are the average heights of steps at grain boundaries.

TABLE 4

SURFACE DEVELOPMENT PRODUCED BY ION MILLING

<u>Sample</u>	<u>Etch Time (Minutes)</u>	<u>Average Thickness of Material Removed (Angstroms)</u>	<u>Surface Relief (Angstroms)</u>
Zinc Selenide	4	800	~ 100
	8	1800	100
	16	2300	100 - 300
	32	4200	200 - 800
Calcium Fluoride	6	~600	50 - 100
	8	~1000	NM
	16	1400	NM
	32	3150	250 - 450

As the surface layers are removed from these polycrystalline materials, the average grain boundary step produced is approximately ten percent of the total thickness removed. The variation of step heights was

somewhat larger for zinc selenide than for calcium fluoride. Although the etch rates for both materials varied somewhat during the experiments (the power supply for the beam was not well stabilized), the average etch rate for zinc selenide was approximately 30 percent higher than that for calcium fluoride.

Figure 20 is a photomicrograph of the zinc selenide sample, taken to include the unetched portions from which the maximum 4200 angstrom layer of material had been removed. Intermediate surfaces were similar but had less distinct grain boundaries. The etched portion contains fine-scale defects such as scratch traces and pitting which are more distinct than those on the unetched portion, as well as the etched polycrystalline microstructure.

The effect of ion milling on the light scattering behavior of the zinc selenide surface is given in Fig. 21. Measurements were made using 6328 angstrom helium-neon laser radiation incident at 45 degrees. The removal of the first two thousand angstroms of material causes an increase of scattering at all angles, probably because both the coarse microstructure relief and the finer polishing-related defects are accentuated. As the etching proceeds, the microstructure relief becomes more pronounced than the finer defects and the low angle scattering increases in intensity more rapidly than the high angle scattering. (Recall that low frequency defects will scatter more strongly at small angles.) After approximately 4000 angstroms have been removed, the scattering between five and ten degrees has increased by a factor of six over the original surface. Some removal of finer defects is indicated by the decrease of the higher angle values relative to less severely etched portions of the specimen.

The scattered intensity increases by approximately fifteen percent at all angles when as much as 2000 angstroms of material are removed from the selenide surface. Certainly no more than this would be removed during any cleaning procedure and a fifteen percent degradation may be taken as a generous upper limit for that produced by ion-beam cleaning.

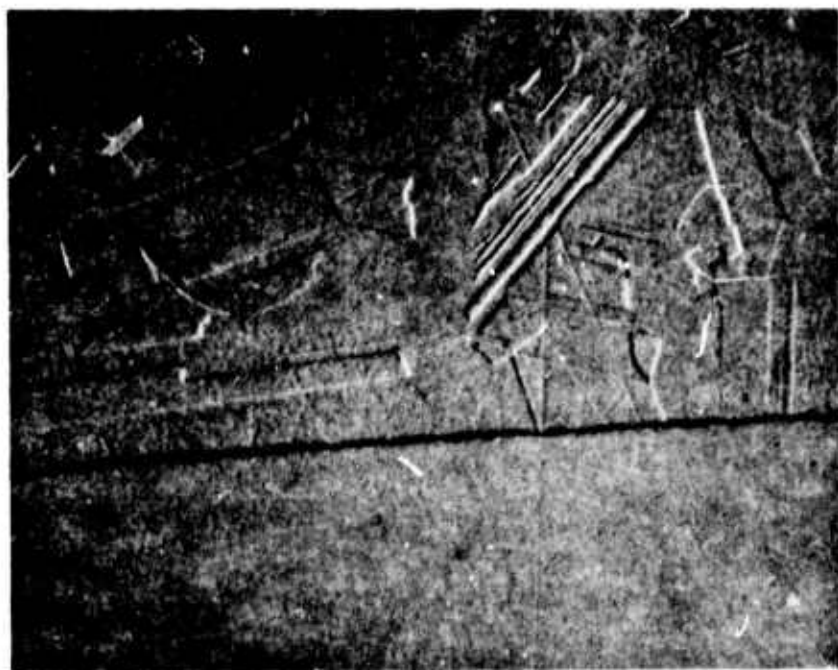


Fig. 20 Microstructure of Ion Beam Polished Zinc Selenide. 766X

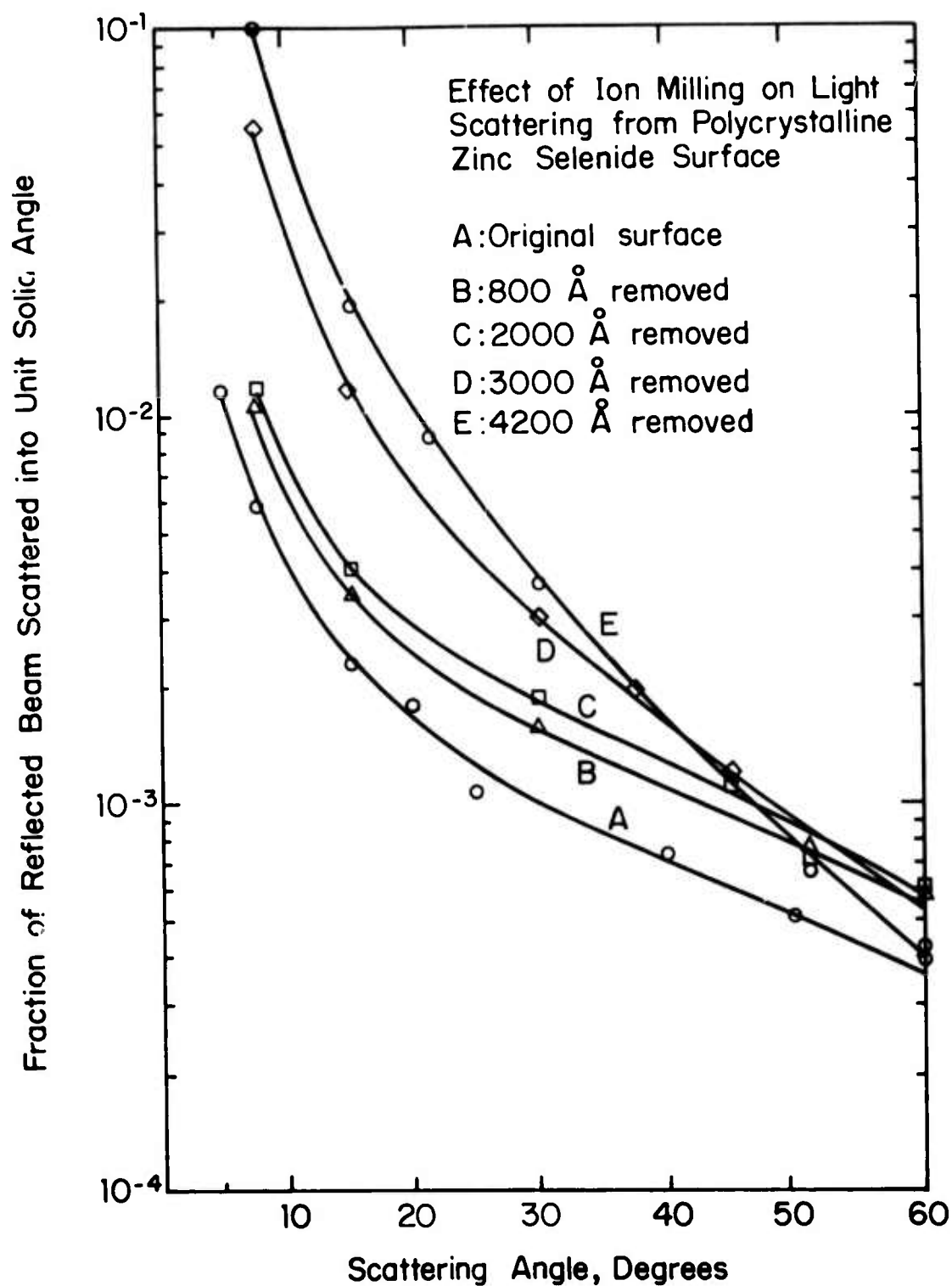


Fig. 21 Light Scattered per Unit Solid Angle vs Scattering Angle - Ion Beam Polished Zinc Selenide Specimens.

2.4 Transparent Abrasive Polishing

Abrasive particles embedded in optical surfaces may be considered to be a universal feature of conventional abrasive polishing. To the extent that they absorb incident laser radiation, they may be sites for preferential damage. One of the surface finishing techniques being assessed by this project is the use of abrasives which are transparent to the laser radiation. When the program was proposed, transparent abrasives were thought to be particularly important for the polishing of components for lasers operating in the 5 to 14 micrometer wavelength range where aluminum oxide and other common abrasive materials are quite opaque. Potassium chloride and zinc selenide were chosen as specimen window materials and zinc sulfide, which is harder than both, as a candidate abrasive material. The third sample material being studied for this program, calcium fluoride, will be used for lasers operating at wavelengths where aluminum oxide itself is a transparent abrasive.

During the first six months of the program, abrasive and chemical surface-finishing procedures for zinc selenide were developed which, although they employed alumina abrasives and required further development, nonetheless raised the zinc selenide damage threshold (at 10.6 micrometers) well above power levels at which thermally-induced optical distortions would limit the usefulness of practical selenide optical elements. Polishing procedures are detailed in the first semiannual report for this project. Damage measurements are presented in the final report for contract number DAAH01-72-C-0194.⁵ The use of zinc sulfide as an abrasive for potassium chloride, therefore, essentially constitutes the transparent abrasive effort.

Zinc sulfide (knoop hardness 250), is approximately 30 times harder than potassium chloride (knoop hardness 8) and is capable of removing stock from chloride surfaces. During the first six months of the program, zinc sulfide abrasives were shown to remove material from potassium chloride surfaces and to produce a rough polish. In this second report period, hardened forms of zinc sulfide were produced and evaluated.

Hardened sulfides were produced by precipitation from aqueous solutions containing intentional impurity additions. Impurity atoms or ions in crystalline materials which cause strains in the lattice immediately

surrounding them make plastic deformation of the material more difficult because the strain fields impede the motion of the dislocations which is responsible for the plastic deformation. In ionic crystals, very substantial hardening effects may be produced by the substitution of ions having a valence which is different from that of the normal lattice ion. Figure 22 illustrates the change in yield point, a physical property closely related to hardness, which is obtained by divalent additions to alkali halides. This is the phenomenon being used to produce strengthened halide window materials. In the case of zinc sulfide, two substitution schemes were attempted for the precipitates; single substitution of trivalent gallium for divalent zinc and double substitution of gallium and monovalent silver for zinc. In the former case, two gallium ions replace three zinc ions; one lattice site remains vacant. The double substitution replaces two zinc ions by a gallium-silver pair. The coupled substitution was attempted because it was expected to be significantly more soluble in the zinc sulfide lattice than the single gallium addition and capable of increased hardening. Zinc sulfide-selenide solid solutions produced as bulk solids by chemical vapor deposition were also evaluated as abrasives after first being ground to appropriate particle sizes.

Pure and hardened sulfides were precipitated in the apparatus shown schematically in Fig. 23. Nitrogen containing ten percent hydrogen sulfide is bubbled through the heated, stirred solution from which the sulfide precipitates. Evaporating water is returned to the reactor by the condenser and excess hydrogen sulfide is trapped in gas scrubbers which contain potassium hydroxide solutions. Pure and gallium-doped zinc sulfides were precipitated from acidic half-molar solutions of zinc chloride to which appropriate gallium chloride additions had been made. Pure zinc sulfide and sulfides containing one-half, one, and two atomic percent of gallium were produced. The gallium-silver substitution was attempted from an acidic nitrate solution because of the insolubility of silver chloride. A ten atomic percent replacement of zinc by gallium/silver was attempted. The extremely low solubility of silver sulfide caused it to precipitate as a separate phase in this case and no doubly substituted material was produced.

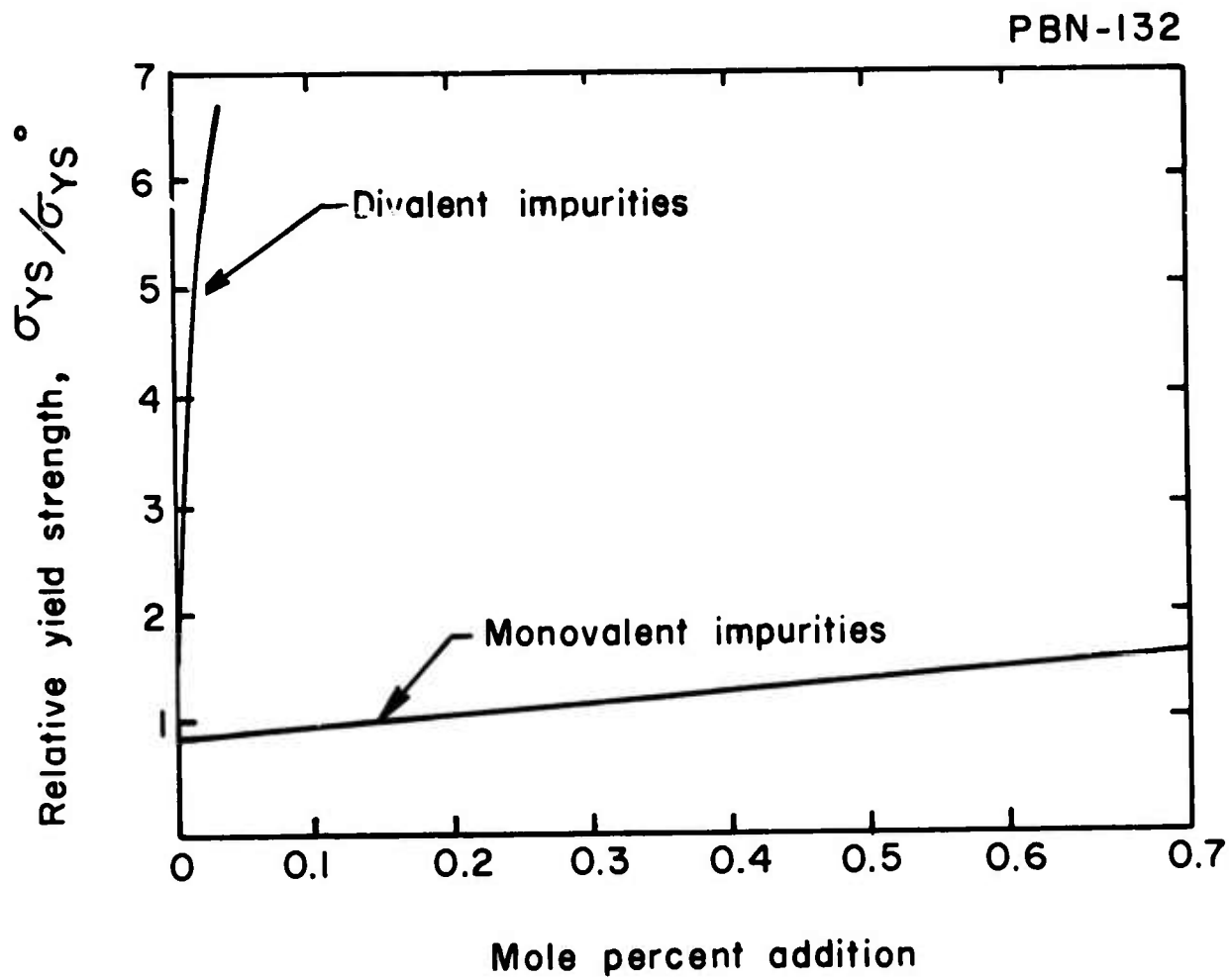


Fig. 22 Hardening Effects of Impurities in Alkali Halides.

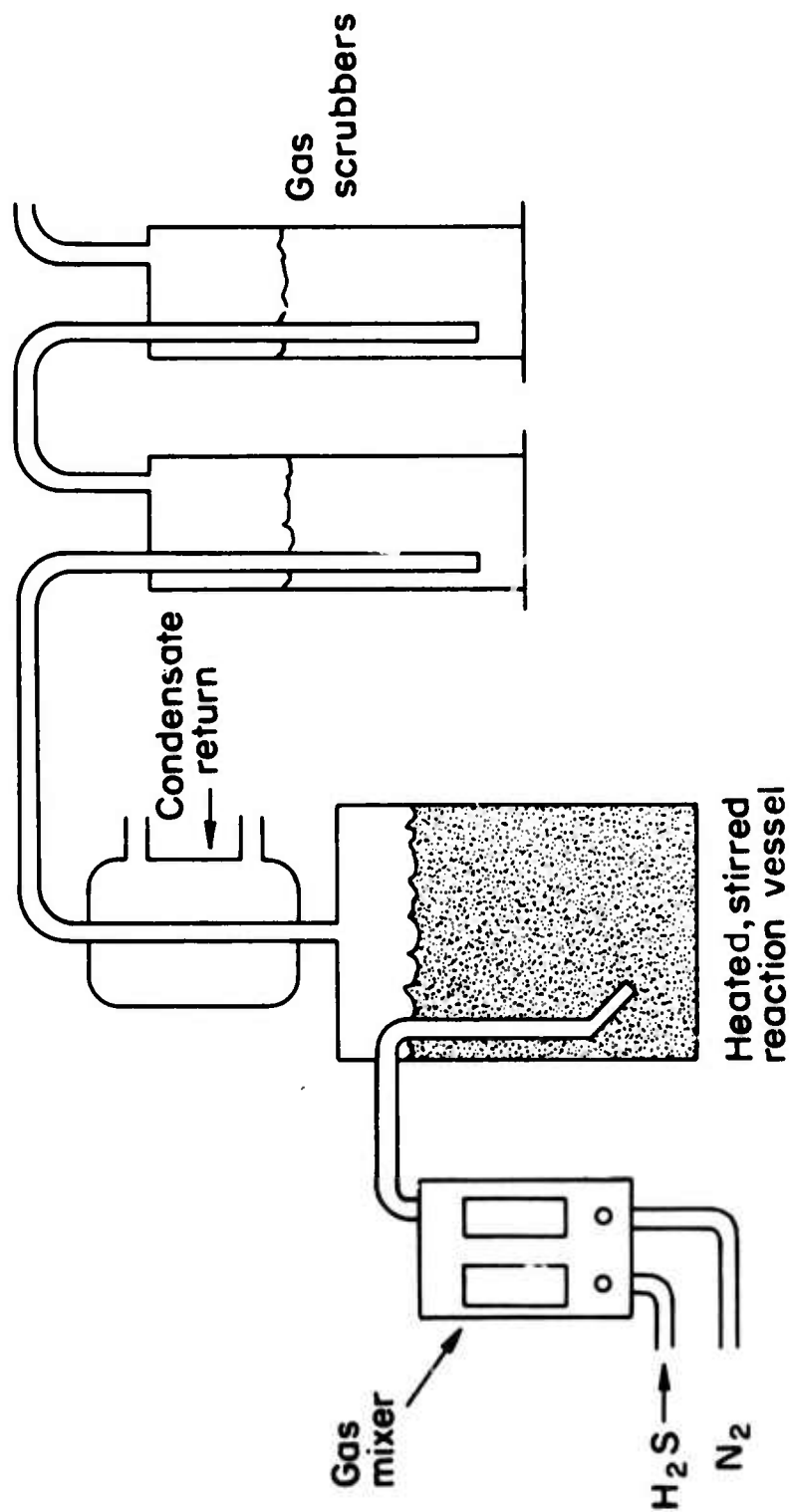


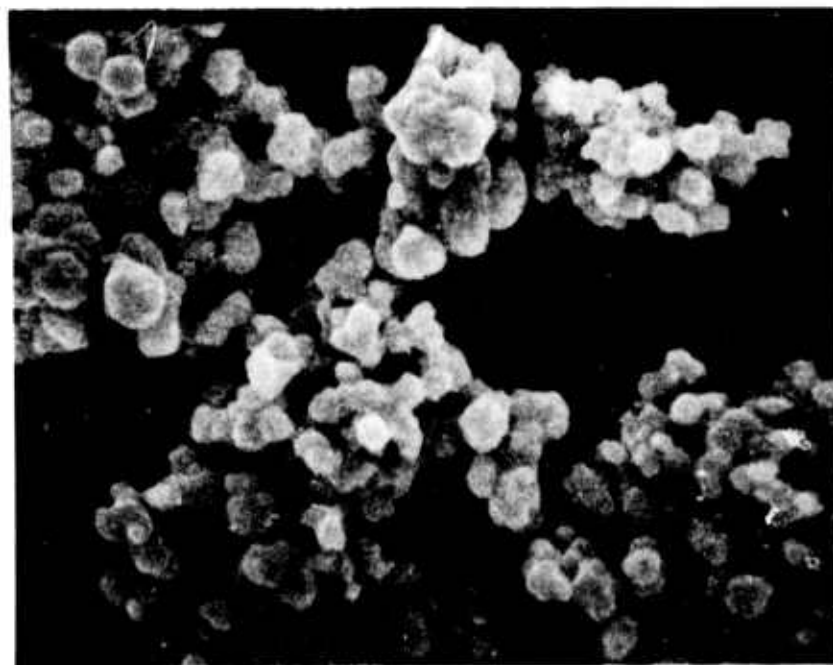
Fig. 23 Precipitator for Zinc Sulfide Preparation.

Pure and gallium-doped zinc sulfide precipitated as more or less spherical particles, one to three micrometers in diameter. Figure 24a is a scanning electron micrograph of as-precipitated pure zinc sulfide. X-ray diffraction analysis of the precipitates showed them to be poorly crystallized mixtures of both the cubic and hexagonal zinc sulfide polymorphs. Heat treatment of the powders improved their crystallinity (as determined by a sharp decrease in the breadth of X-ray diffraction lines) and revealed the polycrystalline character of the precipitated spherulites. Figure 24b is a photograph of a zinc sulfide precipitate annealed in hydrogen sulfide at 600°C for one-half hour.

The pure and the two gallium-doped sulfides were used as-precipitated and after annealing to polish potassium chloride. The polishing was carried out on beeswax laps which were rotated at approximately 30 rpm, using glycerol triacetate (triacetin) as the slurry vehicle. Single crystal and polycrystalline potassium chloride samples were polished. Both hand polishing, in which the work was loaded by only its own weight, and machine polishing, in which the pressure in the material was approximately one-half pound per square inch, were used during the course of the experiments.

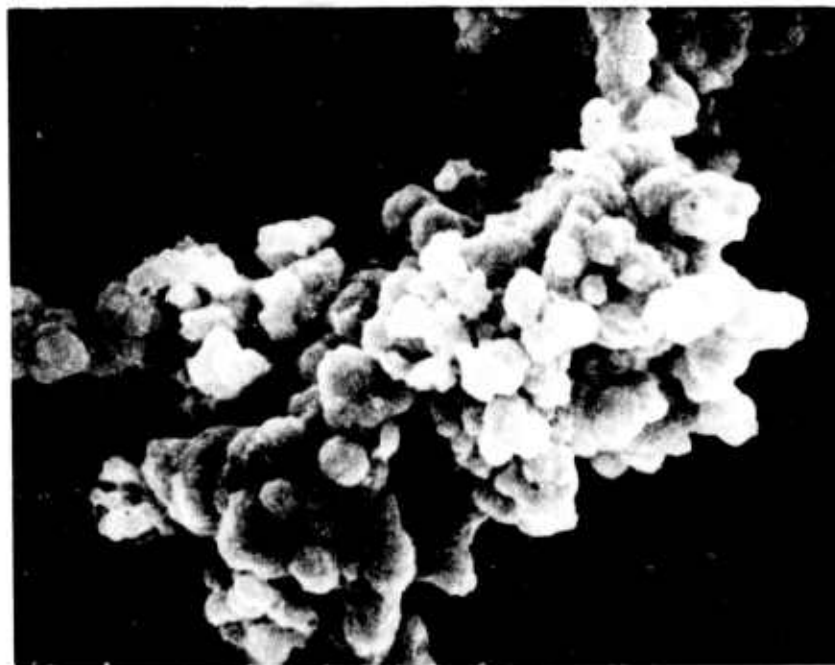
Surfaces produced by the various sulfide materials did not differ significantly. They were generally characterized by scratches on a background of small, irregular digs or pits which were approximately the same size as the abrasive material (a few micrometers in diameter). Figure 25a is a micrograph of a typical zinc sulfide surface on potassium chloride. The rate of stock removal was typically between two and six micrometers per hour for all sulfide materials. No statistically significant correlation between gallium doping level and rate of stock removal or surface quality could be made.

In one instance, a surface comparable to the best polishes obtained by conventional polishing with aluminum oxide was obtained. This surface, shown in Fig. 25b, was produced with annealed zinc sulfide containing two



2 Microns

As Precipitated



2 Microns

After Heat Treatment

Fig. 24 Precipitated Zinc Selenide Abrasives. 5000 \times



b) Best Transparent Abrasive Polished Surface 187x

a) Typical Surface 187x

Fig. 25 Microstructures Produced by Zinc Sulfide Polishing of Potassium Chloride.

atomic percent gallium. The samples were polished for one hour during which time approximately four micrometers of stock were removed. Attempts to repeat the experiment were unsuccessful.

Since surfaces produced by the roughly spherical precipitates may have been in part caused by the particle shapes, zinc sulfide powders containing more angular particles were produced by grinding chemically vapor-deposited material in a ball mill. The coarsest fraction of the particles were removed from the powder by sedimentation and the remaining fine fraction polished potassium chloride specimens to surfaces which were similar to those produced by the spherical precipitates.

Zinc sulfide might be useful as an abrasive for potassium chloride if it were necessary to remove embedded alumina prior to some chemical or chemical-mechanical polishing step which removed surface scratches. Finer sulfide particles would probably produce some surface improvement and other material systems such as hardened alkaline earth fluoride powders might be usefully transparent. It appears, however, that chemical polishing may be used to remove both surface scratches and embedded abrasives from potassium chloride surfaces. Transparent abrasive efforts were terminated during the fourth quarter. The development of chemical techniques which can be applied to large, polycrystalline potassium chloride specimens will be emphasized.

3.0 FUTURE WORK

During the final six months, work in all the active project areas will continue. Particular emphasis will be given to:

a) The determination of the depths of surface damage produced by grinding steps used to fabricate rough blanks. These are likely to be more damaging than the grinding procedures considered in this report.

b) The development of chemical polishing techniques for polycrystalline calcium fluoride and potassium chloride. The techniques sought must permit the controlled etching of large optical elements. Surface features produced by chemical etchants are frequently quite sensitive to minor variations in etch composition or etching techniques; optimized procedures must permit some latitude of application.

The three study materials are different chemically and their etching may be expected to reflect the differences. Zinc selenide is etched in an oxidation-reduction reaction, potassium chloride by dissolution. Calcium fluoride is also etched by dissolution, but the calcium ions may be bound up in insoluble surface layers in some etchant solutions. During the final six months of the program, a major effort will be made to develop an understanding of the mechanisms of the processes, taking into account both the polycrystalline character of the specimens and the chemical differences among them.

c) The independent evaluation of surfaces generated by optimized techniques. Samples will be submitted to the Naval Weapons Center, China Lake, California for FECO and Surface Scattering measurements. Laser damage measurements will be made on potassium chloride specimens.

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